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The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 70 Number 9

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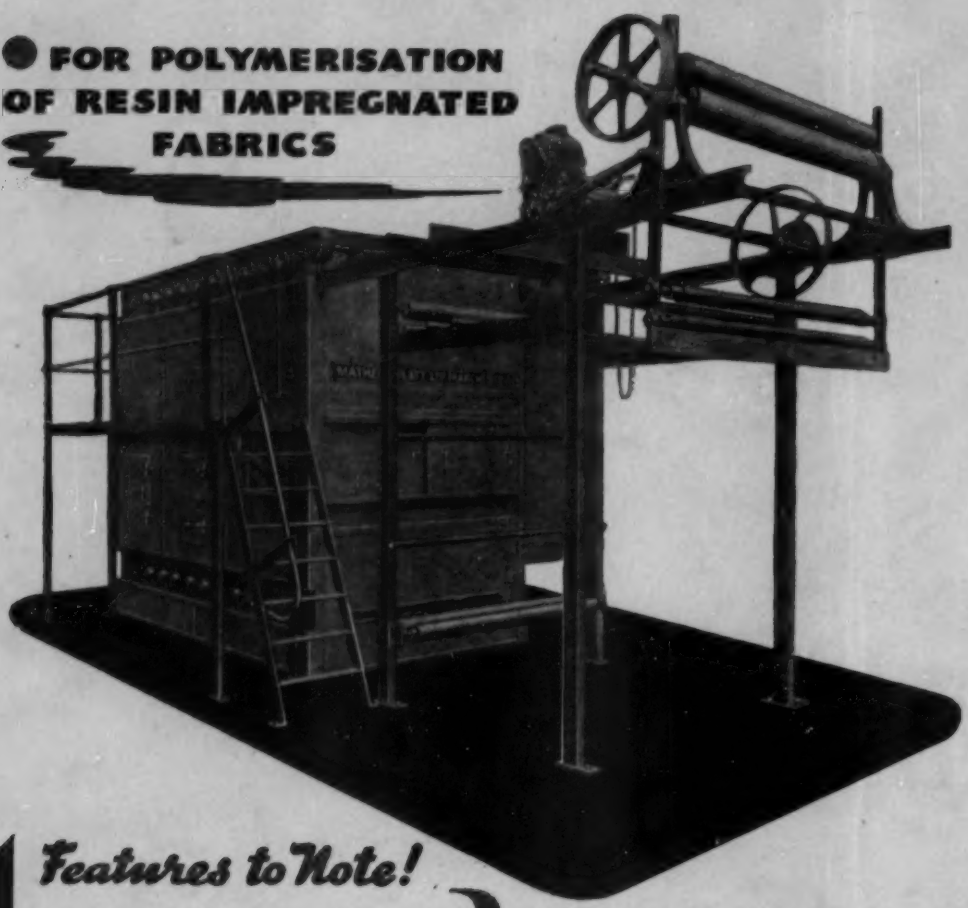

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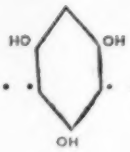

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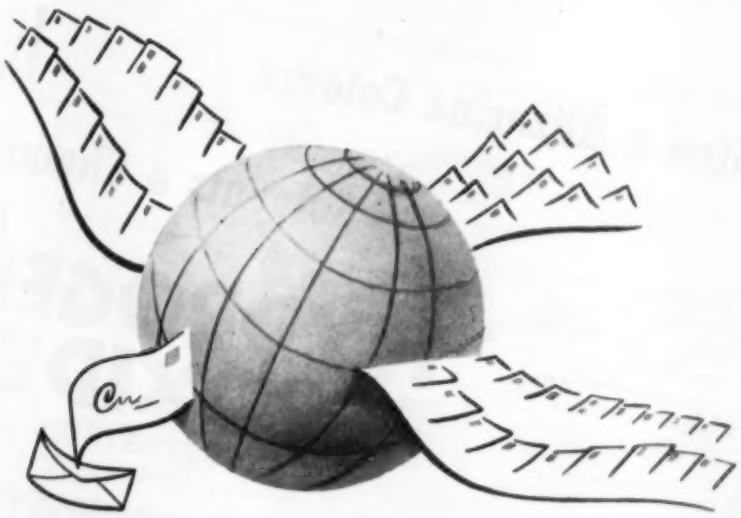

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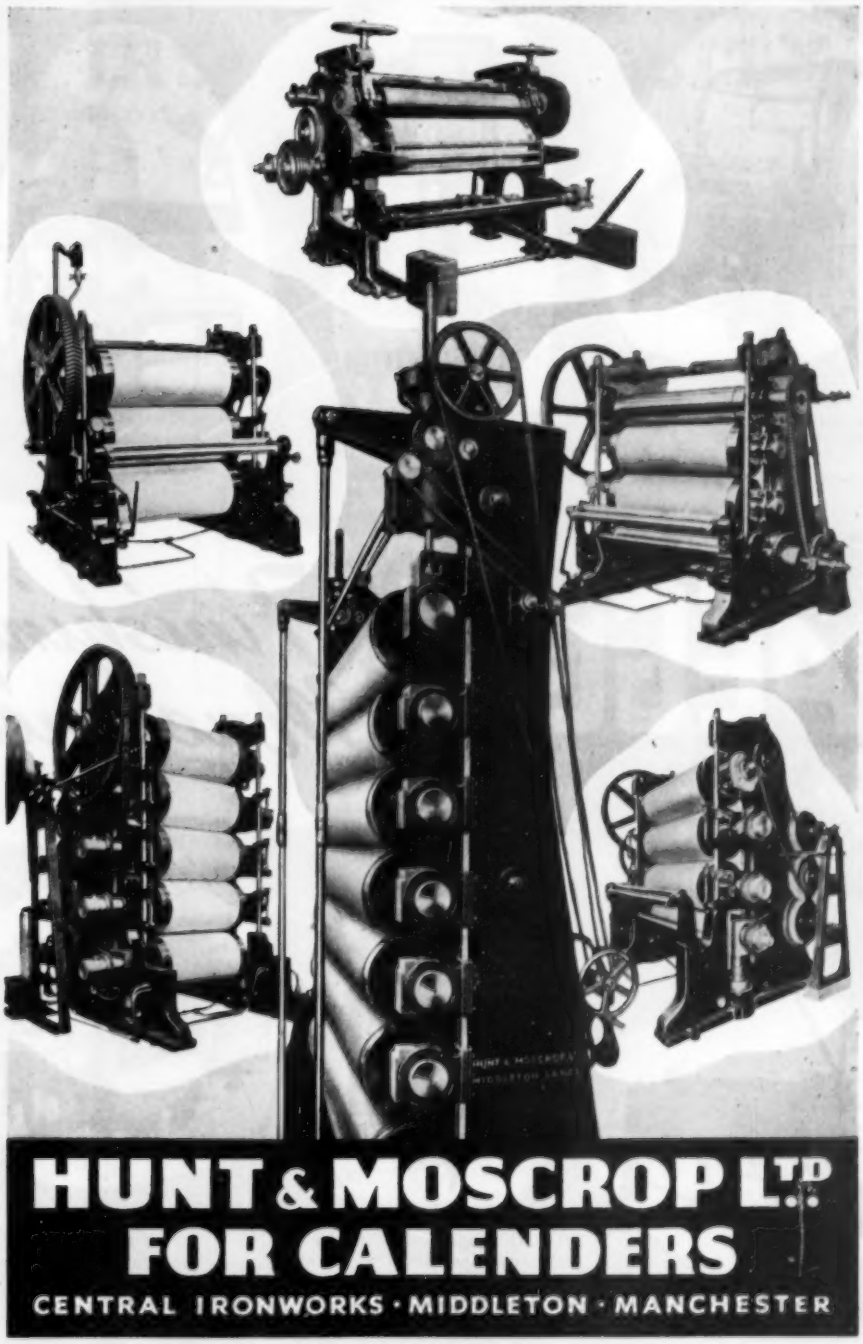
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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1954 and pages 262–266 of the July 1954 issues of the *Journal*, or write to *The Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Azoic Dyes on Acetate Rayon — *I. M. S. Walls*

Some Applications of *iso*Cyanates — *G. S. J. White*

COMMUNICATIONS

The Polarography of Azo Dyes — *J. de O. Cabral and H. A. Turner*

Researches upon the Light Fading of Dyes— II — *H. R. Chipalkatti, C. H. Giles, et al.*

Qualitative and Quantitative Analysis of Vat Dyes by Paper Chromatography — *E. Klingsberg*

The Histology of Keratin Fibres — *B. Manogue, M. S. Moss, and R. L. Elliott*

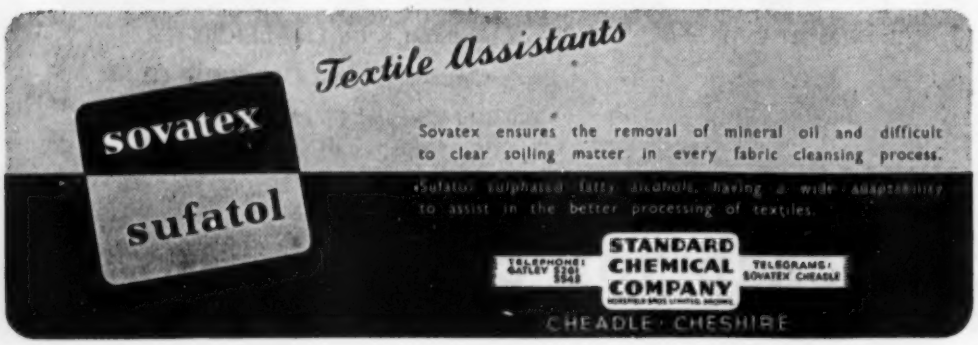
Dyeing of Cellulose Acetate with Non-ionic Dyes— I and II — *T. G. Majury*

The Combination of Keratin with Acids — *L. Peters*

Some Factors in the Measurement of Affinities of Vat Dyes for Cellulose — *R. H. Peters and J. Simons*

F.T.C.C. PUBLICATION

The Use of Fading Lamps for Determining Light Fastness — *K. McLaren*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FORTHCOMING MEETINGS OF THE SOCIETY

PERKIN MEDAL AWARD

The award of the Perkin Medal to Dr. Arthur Zitscher will take place at 7 p.m. in the Large Chemistry Lecture Theatre, University of Manchester, on Friday, 15th October 1954. Dr. Zitscher will then deliver a lecture on the subject relating to his award — For his Work leading to the Discovery of the New Class of Azoic Dyes, based on the Arylamides of *o*-Hydroxycarboxylic Acids.

Tuesday, 28th September 1954

SCOTTISH SECTION. *Is Dyeing Theory of any use to the Practical Dyer?* Dr. L. Peters (Lecturer in Textile Industry, Leeds University). St. Enoch Hotel, **Glasgow.** 7 p.m.

Friday, 1st October 1954

LONDON SECTION. *The Wear Properties of Resin Treated Fabrics.* Dr. T. H. Morton (Courtaulds Ltd.). Royal Society Rooms, Burlington House, **London, W.1.** 6 p.m.

Wednesday, 6th October 1954

MIDLANDS SECTION. *The Dyeing of Wool at High Temperatures.* D. R. Lemin, Esq., B.Sc., H. Sagar, Esq., A.T.I., F.I.C., and G. A. Coutie, Esq., B.A., (Mr. Lemin lecturing). College of Technology, **Leicester.** 7 p.m.

Wednesday, 13th October 1954

NORTHERN IRELAND SECTION. *Economic, Technical and Other Difficulties in Meeting Fastness Requirements.* S. Burgess, Esq. (Courtaulds Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Friday, 15th October 1954

Lecture by Dr. A. Zitscher in **Manchester** (see above).

WEST RIDING SECTION. Supper and Smoker. Victoria Hotel, Bridge Street, **Bradford.** 7 p.m.

Tuesday, 19th October 1954

SCOTTISH SECTION. *Some Notes from a Rayon Piece Dyer's Note-book.* C. C. Wilcock, Esq., A.R.T.C.S., F.T.I., F.S.D.C. (Courtaulds Ltd.). St. Enoch Hotel, **Glasgow.** 7 p.m.

Thursday, 28th October 1954

WEST RIDING SECTION. *Incidents during 43 years Research.* Dr. H. H. Hodgson, Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

MIDLANDS SECTION. Discussion on *Dyeing Machine Design.* Opening Speaker — F. H. Marsh, Esq., B.Sc., F.R.I.C. Gas Theatre, **Nottingham.** 7 p.m.

Friday, 5th November 1954

LONDON SECTION. *Fabric Faults and Unserviceable Accessories.* J. H. Moulder, Esq., B.Sc. (Assistant Director of the Dyers and Cleaners Research Organisation). Joint meeting with the Guild of Dyers and Cleaners (London Centre). Royal Society Rooms, Burlington House, **London W1.** 6 p.m.

Wednesday, 10th November 1954

NORTHERN IRELAND SECTION. *Some Observations on American Bleaching and Dyeing Processes.* J. K. Skelly, Esq. (Belfast College of Technology). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 11th November 1954

WEST RIDING SECTION. *The Dyeing of Leather.* D. Woodroffe, Esq., M.Sc., A.R.I.C. (Head of Leather Department, Northampton College of Technology). Hotel Metropole, **Leeds.** 7.30 p.m.

Tuesday, 16th November 1954

SCOTTISH SECTION. *Silicones in the Textile Industry.* T. W. Watson, Esq., B.Sc. (Midland Silicones Ltd.). St. Enoch Hotel, **Glasgow.** 7 p.m.

Wednesday, 17th November 1954

MIDLANDS SECTION. *Dyeing of Terylene above 100°C.* A. S. Fern, Esq., B.Sc., F.S.D.C. Kings Head Hotel, **Loughborough.** 7 p.m.

Friday, 19th November 1954

MIDLANDS SECTION. *Colour fastness from the point of view of the Manufacturer, Dyer and Consumer* (Forum) (Joint meeting with the Leicester Textile Society and Textile Institute). College of Technology, **Leicester.** 7 p.m.

Saturday, 20th November 1954

MIDLANDS SECTION. LADIES EVENING — DINNER DANCE. Black Boy Hotel, **Nottingham.** 7 p.m.

Thursday, 25th November 1954

WEST RIDING SECTION. *The Fixation of Direct Dyestuffs.* Dr. R. Gill (Allied Colloids Ltd.). Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Wednesday, 1st December 1954

MIDLANDS SECTION. *The Evaluation of Optical Bleaching Agents.* G. G. Taylor, Esq., B.Sc., A.Inst.P. (Joint meeting with the British Association of Chemists). College of Art, **Derby.** 7 p.m.

Friday, 3rd December 1954

LONDON SECTION. *The Dyeing of Textile Fibres at Temperatures above 100°C.* Mr. J. A. Fowler (I.C.I. Ltd.). Royal Society Rooms, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 7th December 1954

SCOTTISH SECTION. *Electrical Aids to Production in the Textile Industry.* L. Landon Goodman, Esq., B.Sc. (British Electrical Development Association). St. Enoch Hotel, **Glasgow.** 7 p.m.

Wednesday, 8th December 1954

NORTHERN IRELAND SECTION. *Some aspects of Design in Bleaching and Finishing Plant.* W. W. Spooner, Esq. (Spooner Dryer and Engineering Co. Ltd.). (Joint Meeting with Foremen Dyers' Guild). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 9th December 1954

WEST RIDING SECTION. *Oriental Printing Methods and Prints.* R. Thornton, Esq., B.Sc. (I.C.I. Ltd.). Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Thursday, 6th January 1955

NORTHERN IRELAND SECTION. *The Modern Approach to Linen Bleaching and Finishing* I. M. Hill, Esq. (Milltown Bleaching Co. Ltd.) (Joint lecture with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Friday, 7th January 1955

LONDON SECTION. Details later.

Wednesday, 12th January 1955

NORTHERN IRELAND SECTION. *Application and Evaluation of Optical Bleaching Agents.* Messrs. G. Taylor and A. V. Cole (Clayton Dyestuffs Co. Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Wednesday, 26th January 1955

MIDLANDS SECTION. *I do it this way!* Demonstrations of novel testing techniques by local members. College of Technology, **Leicester.** 7 p.m.

Friday, 28th January 1955

LONDON SECTION. Annual Dinner Dance at The Waldorf Hotel, **London WC2.**

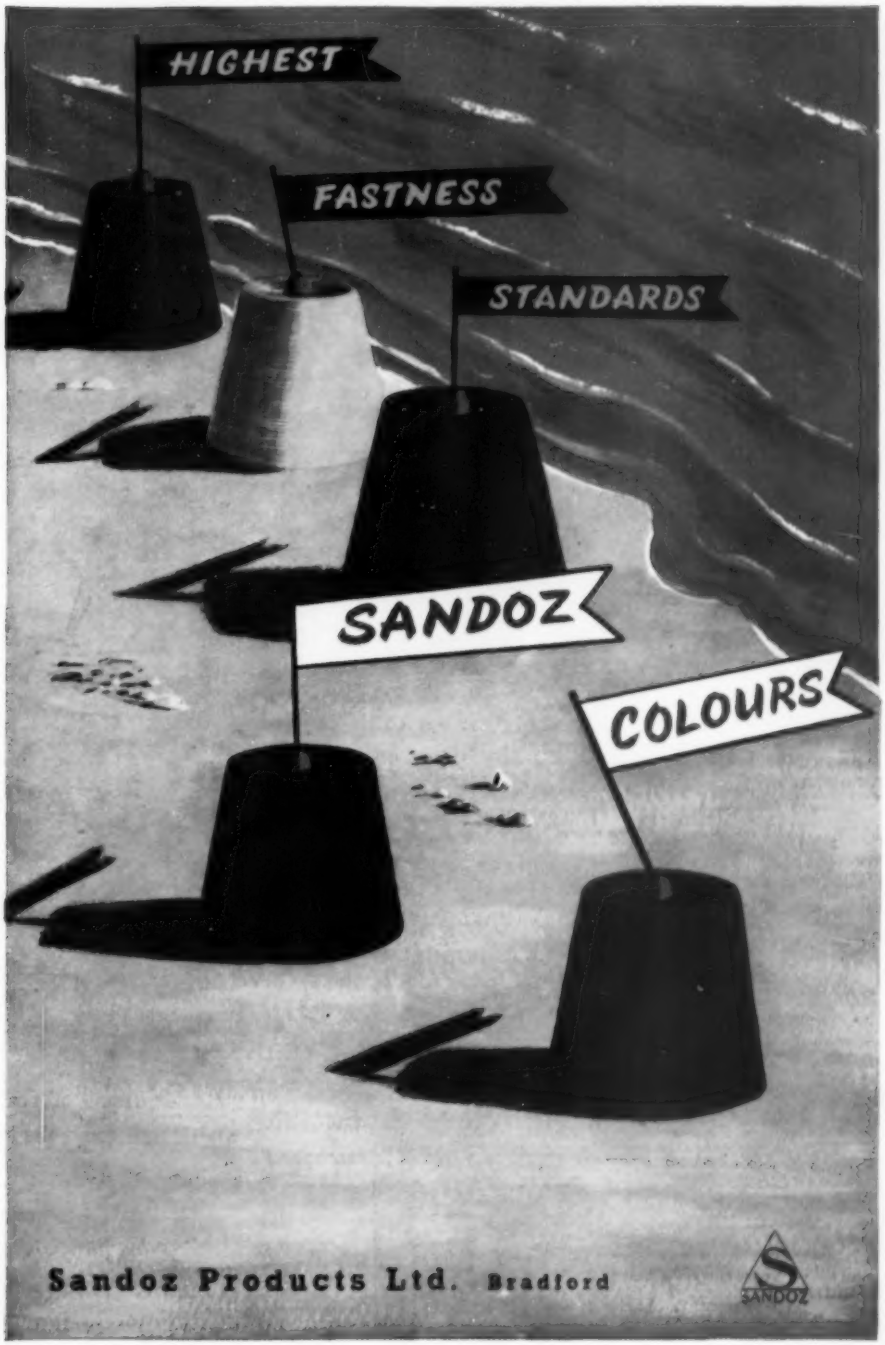
Friday, 4th February 1955

LONDON SECTION. *Textile Performance Standards for the Distributor.* Messrs. F. Cowles and J. S. Ingham (Marks and Spencer Ltd.). Royal Society Rooms, Burlington House, **London W1.** 6 p.m.

Wednesday, 9th February 1955

NORTHERN IRELAND SECTION. *Fastnesses of Coloured Textiles as they Affect the General Public.* J. S. Ingham Esq. (Marks & Spencer Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

continued on page xxxiii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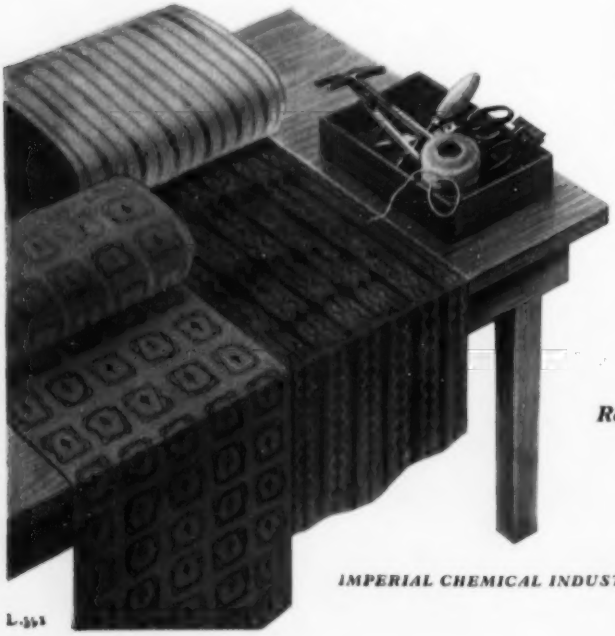

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THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 70 Number 9 SEPTEMBER 1954 *Issued Monthly*

Proceedings of the Society

The Application of Resins to Textiles

A. R. Smith

Meeting of the West Riding Section held at the Victoria Hotel, Bradford, on 25th February 1954, Mr. G. B. Angus in the chair

The nature of thermoplastic and thermosetting resins is discussed together with the chemical reactions involved in their preparation. The application of thermosetting resins to cellulosic fabrics for the production of crease-resistant, dimensionally stable, and permanently glazed and embossed fabrics is outlined, while their use for the prevention of felting in wool fabrics and for the permanent stiffening of various types of textile materials is also considered. The use of thermoplastic resins in the treatment of textiles is discussed, and finally a number of special applications of synthetic resins in the production of permanent showerproof, fire-resistant, and other finishes is briefly outlined.

INTRODUCTION

Every year, the variety of printed, woven, and other effects produced by the textile industry increases, and at the same time the range of wash-fast types of textile finish becomes more extensive. In this respect the textile trade owes something to the plastics industry, for it is frequently in the development of plastic materials for other purposes that new and permanent textile finishing agents have been evolved. (The word "permanent" as employed in this paper is a relative term and implies only that the finish will remain substantially unchanged during the normal life of the fabric.)

It is difficult to define the term "plastics" with accuracy, but, broadly speaking, the name is applied to substances which flow under heat and pressure, and which are produced from simpler starting materials by chemical reaction. Plastics are generally subdivided into thermoplastic and thermosetting materials, the former being repeatedly deformable under heat and pressure, while the latter, although flowing under the initial heating and pressing operation, undergo further chemical changes during this operation, so that subsequent deformation is no longer possible.

Thermoplastic materials include the polyvinyl derivatives, cellulose acetate, nylon, and Terylene. The condensation products of formaldehyde with phenol, urea, melamine, and similar compounds are thermosetting. Rubber may be regarded as thermoplastic in its natural form, while its vulcanisation is a thermosetting process.

The above definitions of thermoplastic and thermosetting resins are more accurately applicable when these products are used for the production of moulded articles. In textile finishing, thermoplastic resins are most frequently employed for producing firmness of handle in the fabric, and for this purpose are applied as an emulsion of the polymerised product. No further polymerisation is required after their application, and the characteristic of such finishes is that they soften at increased temperatures. Thermosetting resins, on the other hand, are usually applied as precondensates, and further condensation on the fabric is necessary if a permanent wash-fast finish is to be obtained.

The subject of this paper is a wide one, and it is proposed to deal mainly with the uses in textile finishing of urea- and melamine-formaldehyde resins, which find more extensive application than other plastic materials. The principal uses of other synthetic resins in the textile industry will also be referred to where possible. It is proposed to consider the subject under the following headings—

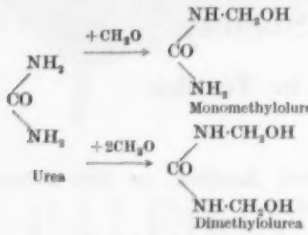
1. Crease-resistant and shrink-resistant finishes on cellulosic fabrics
2. Permanent glazed or embossed finishes on cellulosic fabrics
3. Shrink-resistant finishes on wool
4. Permanent stiffened finishes on cellulosic fabrics
5. Improvement of colour fastness

6. Pigment printing and padding
7. Miscellaneous applications of resins.

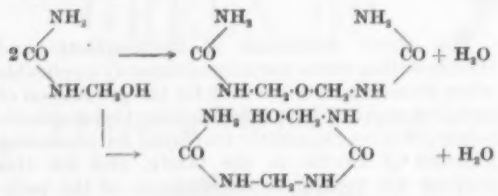
Before discussing these applications of synthetic resins, however, it is advisable to consider the chemical nature of the materials involved, and for this purpose the principal reactions which take place during the production of some typical plastics or synthetic resins will first be outlined.

(*a*) *Urea–Formaldehyde Resins*

The reaction between urea and formaldehyde in neutral or alkaline solutions results primarily in the production of mono- or di-methylolurea (mono- or bis-hydroxymethylurea)—



These compounds are very reactive and their isolation in a pure state is extremely difficult. During the drying of such materials, for example, further reaction can take place with elimination of water. Thus monomethylolurea may undergo the following reactions—



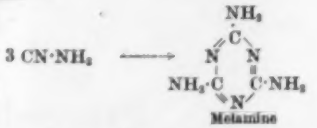
Similar reactions can take place with dimethylolurea, and, since some free formaldehyde is also invariably present, highly complex reaction products can be produced. It is consequently found that the drying of methylolureas at high temperatures results in products of very low solubility in water, although the pure methylol compounds are highly soluble. Drying at low temperatures gives a product of lower complexity and higher solubility, but the material is still too far condensed for use in such applications as the crease-resisting of textiles. Even in dilute solutions, these types of reaction are constantly proceeding and consequently the material in solution is continually changing in composition.

In order to produce a reliable commercial material of reasonable stability for textile applications, some modification of the above reaction must be made. Two suggested processes have been the methylation of dimethylolurea to give the stable, crystalline dimethyl ether [1], and the modification of the reaction mixture by addition of hexamine. In either case a highly water-soluble material is produced with a storage life of several months.

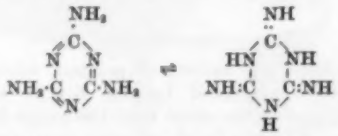
By reaction with butanol instead of methanol under suitable conditions, butylated resins or butyl ethers of the methylol compounds may be prepared [2]. These are "solvent-soluble" and are used in the production of synthetic stoving enamels. In emulsion form they find use in pigment printing and padding on textile materials.

(*b*) *Melamine–Formaldehyde Resins*

Melamine may be regarded as the trimer of cyanamide—



Reaction of melamine with formaldehyde under neutral or alkaline conditions results, as with urea, in the production of methylol derivatives, and compounds of one molecule of melamine with 2–6 molecules of formaldehyde have been reported. The production of hexamethylolmelamine would involve the reaction of both hydrogen atoms of each amino group in the above formula for melamine, and would not therefore be analogous to urea, where only one hydrogen on each amino group is reactive, although derivatives of tetramethylolurea have been prepared by indirect methods. A suggested explanation of this anomaly is that melamine really consists of two or more structural forms in dynamic equilibrium, e.g.—



The drying of the methylolmelamines is accompanied by further condensation as with the methylolureas, and the drying of tetra-, penta-, and hexa-methylolmelamine is also accompanied by progressively increasing loss of formaldehyde. Stabilisation may again be effected by methylation, and the hexamethyl ether of hexamethylolmelamine has been found to be quite stable [3]. These methyl ethers are the form in which commercial melamine–formaldehyde precondensates are usually offered to the textile industry, although complete methylation is not normally attained. A sufficient degree of methylation to restrict the condensation of the material and give an adequate storage life is all that is required.

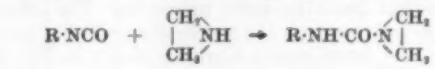
In the case of melamine and formaldehyde, the structure of the compounds produced is even more complex than with urea, and a corresponding increase in the wash-fastness of the finally cured resin on the textile fabric is achieved. Solvent-soluble resins are again obtained by butylation.

(*c*) *Other Formaldehyde-based Resins*

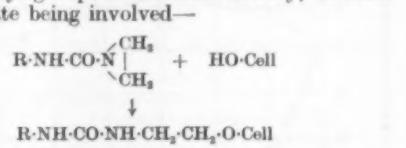
Many other amino compounds react with formaldehyde to form similar complexes, and of these cyanamide [4], dicyandiamide [5], guanidine [6], ethyleneurea [7], and acetylenediurea [8] have been exploited commercially. Of other formaldehyde

condensation products, those with acetone [9] and glyoxal [10] have aroused considerable interest.

Cyanamide, dicyandiamide, and guanidine resins have been particularly advocated for improving the wash-fastness of direct dyes or conferring affinity for acid dyes on cellulose. It should be mentioned that two different types of ethyleneurea derivatives have been suggested for the treatment of cellulosic textiles. One type is produced by the reaction of *iso*cyanates with ethyleneimine [11] and was developed in Germany during the 1939–1945 war—

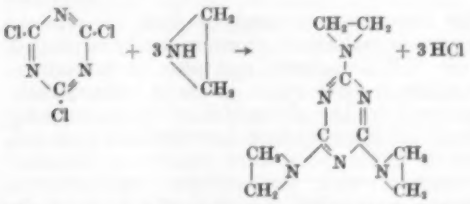


Compounds of this type are not used in conjunction with formaldehyde, but are claimed to react with the hydroxyl groups of cellulose directly, no resin intermediate being involved—



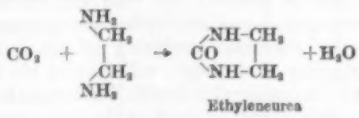
The group R in these compounds may be a long carbon chain, in which case permanent water-repellency is imparted to the cellulosic material. Other compounds of this series have been used for the production of crease-resistant or shrink-resistant fabrics.

A product formed in a similar manner from cyanuric chloride and ethyleneimine is triethylene-melamine [12]—

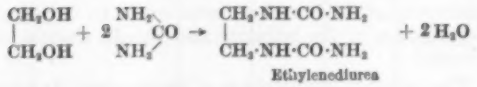


This compound is claimed to react with cellulose at temperatures as low as 70°C. with the production of crease-resistant and shrink-resistant effects.

An entirely different type of ethyleneurea is produced by the reaction of ethylenediamine with carbon dioxide [13] or of glycol with urea or ammonium carbonate [7]—



Ethyleneurea



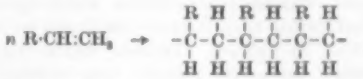
Ethylenediurea

These compounds form methylol derivatives with formaldehyde which behave similarly to other amino-resin precondensates.

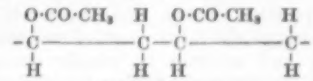
(*d*) *Polyvinyl Resins*

The types of resin described above are all thermosetting and their final condensation involves a loss of water. Their structure is three-dimensional and extremely complex in the final stages.

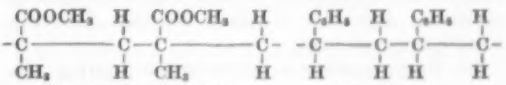
Polyvinyl resins, on the other hand, are produced by an addition reaction as opposed to a condensation, and the products are thermoplastic and linear in constitution. It is to this class that many synthetic fibres belong, including Saran, Vinyon, and Orlon. The general reaction which occurs in the production of these polymers is as follows—



For textile applications, the material is applied to the fabric as an emulsion of the completely polymerised material [14]. It is usually produced by emulsion polymerisation of the monomer, the emulsion, containing a suitable catalyst such as benzoyl peroxide, being heated until the reaction is complete. The polymer emulsion (usually about 50% solids) is then suitably diluted for application to the fabric, and applied by padding and drying, no heat-curing treatment being necessary. The polymers of this type most frequently employed in textile finishing are polyvinyl acetate, polymethyl methacrylate, and polystyrene—



Polyvinyl acetate



Polymethyl methacrylate Polystyrene

1. CREASE-RESISTANT AND SHRINK-RESISTANT FINISHES ON CELLULOSIC FABRICS

The original T.B.L. (Tootal Broadhurst Lee Co. Ltd.) patents [15] accurately specified the requirements for the production of a permanently crease-resistant finish on cellulosic fabrics. It was emphasised in these patents that the resin employed should penetrate the cellulose fibres and that surface resin was undesirable. Urea–formaldehyde or phenol–formaldehyde condensation products were suggested, and the need for these products to be of low molecular complexity, so as to enter the structure of the cellulose, was clearly appreciated.

The fibres of natural or regenerated cellulose contain crystalline and amorphous regions [16], of small dimensions in relation to those of the fibres themselves and arranged at random. In the crystalline regions, the long-chain cellulose molecules are arranged in parallel formation and the close-packed structure tends to favour cross-linking by secondary valencies, so that the conditions do not encourage penetration by substances from the surrounding medium. The amorphous regions, on the other hand, contain cellulose molecules arranged in a haphazard manner, and these regions are permeable to solutions of dyes or synthetic resins. There is, however, a limit to the size of molecules that can penetrate the structure, and this suggests an

explanation of the difficulty experienced in dyeing with dyes of large molecular size and at the same time shows the importance of using resins in a low state of condensation to ensure adequate penetration of the cellulose.

The solution and reprecipitation of cellulose in the manufacture of viscose rayon results in a product of lower average molecular weight and an increase in the proportion of amorphous material in the fibre. Viscose rayon fibres which have been stretched during manufacture are found to be more crystalline in nature. Cotton which has been mercerised tends to become less crystalline in structure, and more nearly approaches regenerated cellulose in its proportion of amorphous material.

The swelling of cellulose in water is also influenced by its degree of crystallinity, the secondary valencies in the crystalline regions tending to resist the expansion of the fibre in the water. It is therefore to be expected that the ratio of wet to dry tensile strength will be higher for cotton and linen than for viscose rayon.

The penetration of resin precondensates is therefore limited to the amorphous regions of the cellulose fibres and is also conditional on the molecular dimensions of the precondensate. The surface deposition of such resins invariably results in a stiffening of the fabric, loss of crease-resistant properties, and a drop in tensile strength. A theoretical explanation of the observed effects of amino-resin treatments on the tensile strength of cellulose may be reached if the following assumptions are made—

(*a*) Resin molecules below some limiting size penetrate the amorphous regions of cellulose fibres and increase their tensile strength, but do not penetrate the crystalline regions, which are decreased in strength by a surface coating of resin.

(*b*) Resin molecules above this limiting size do not penetrate the amorphous regions and are therefore deposited entirely on the surface of the fibres, thus producing a decrease in tensile strength in both the crystalline and amorphous regions.

A complete picture can then be built up of the effect of resin treatment on the tensile strength of cellulose.

Fibres such as cotton or linen have a high proportion of crystalline regions and are lowered in tensile strength by amino-resin treatment, any increase in tensile strength in the amorphous regions being outweighed by the greater decrease in strength in the crystalline regions. This average decrease in tensile strength is reduced by processes, such as mercerisation, which increase the percentage of amorphous material, or by aftertreatment with acid or alkaline solutions, which tend to strip surface resin preferentially from the fibres. Resin treatment of viscose rayon, on the other hand, results in an average increase in tensile strength of the fibre, provided that the resin molecules are small enough to penetrate the amorphous regions: the increase in tensile strength in these regions more than counterbalances the decrease in strength in the crystalline regions. This increase in tensile strength does not occur if surface resin is deposited on the fibres, whether this is due to the employment of an overcondensed resin solution or to unsatisfactory processing conditions resulting in migration of resin to the surface. Surface resin is invariably detrimental to the handle obtained, the crease-recovery of the fabric, and its tensile strength. When the state of condensation of the resin has been satisfactory and surface resin has been formed owing to migration during drying, the crease-recovery may be improved and the handle of the fabric softened by vigorous soaping or mechanical breaking-down operations. The effect of resin treatment on the tensile strength of typical cotton and rayon staple fabrics is shown in Fig. 1.

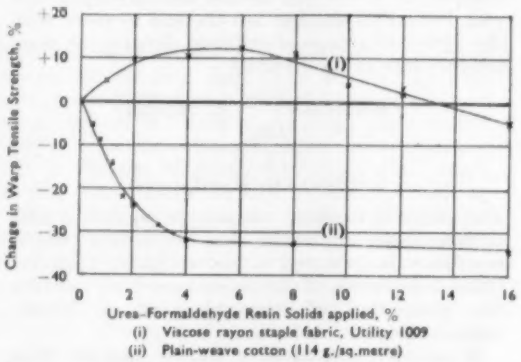


FIG. 1—Effect of Resin Treatment on Tensile Strength of Cellulosic Fabrics

The above remarks apply to both the phenol– and urea–formaldehyde resins originally advocated in the T.B.L. patents and also to melamine–formaldehyde and other products subsequently introduced for the production of crease-resistant finishes. All these products have formaldehyde as a common factor, and some degree of chemical combination with the cellulose molecules is probably responsible for the effect on tensile strength. Thermoplastic resins, such as polyvinyl acetate, which are highly polymerised before application and therefore result in a surface coating of the fibres, do not affect the tensile strength of cellulose in the same way, and this may well be due to their lack of chemical reactivity.

It should be pointed out that the decrease in tensile strength associated with resin treatments is not due to chemical tendering of the cellulose, since stripping of the resin will restore the tensile strength to its original value [17]. Faulty make-up of the resin bath, however, such as the use of excessive quantities of accelerators, may result in chemical degradation of the cellulose and should always be avoided.

The practical application of crease-resist finishes is usually carried out as follows—

The concentration of the resin solution is adjusted so that, after allowing for the expression of the mangle employed, 10–15% of resin solids is applied to the fabric. A catalyst must then be added to the solution to effect the final cure of the resin, and this may be an acid or a substance which

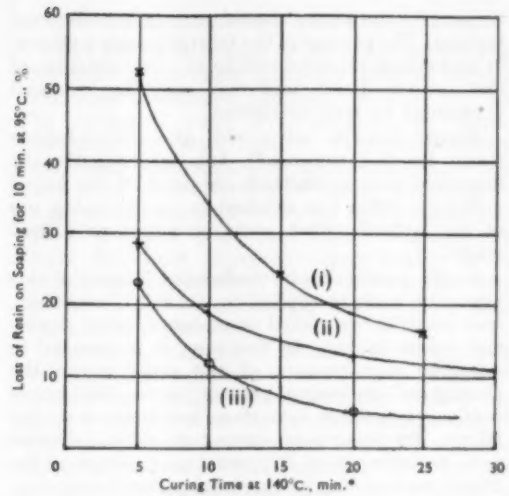


FIG. 2—Effect of Choice of Accelerator on Curing Rate of Urea–Formaldehyde Resin

will produce acidic conditions during the final baking of the fabric (see Fig. 2–4). It is preferable to use such "potentially acid substances", and many types of catalyst have been suggested in the patent literature, ammonium salts being most extensively employed [18]. These are capable of reacting with free formaldehyde in the resin to give hexamine and the free acid and thus lead to the acidic curing conditions required. Other suggested catalysts have been hydrogen peroxide [19] and salts of complex organic bases [20].

After addition of the catalyst, the fabric is padded through the resin solution, dried, and subjected to a final heat-curing treatment such as

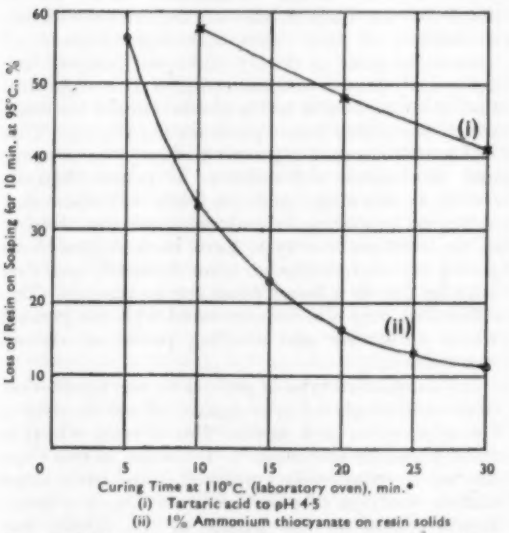


FIG. 3—Effect of Choice of Accelerator on Curing Rate of Urea–Formaldehyde Resin

* These times are based on laboratory conditions and should be halved in works practice to give comparable results.

3 min. at 140°C. The mangle expression should be as low as possible to reduce the quantity of water to be subsequently removed in drying. Adequate penetration of the resin solution is assisted by addition of a wetting agent to the padding bath and by the use of a double dip and double nip, particularly in the case of heavier or less absorbent fabrics. An air passage after mangling and before drying also assists in this respect, and the actual drying operation should be arranged so as to minimise resin migration. For this reason stenter drying with hot air applied equally to both surfaces of the fabric is almost essential. A pin stenter is preferred to a clip stenter, since migration in the vicinity of the clips is liable to occur.

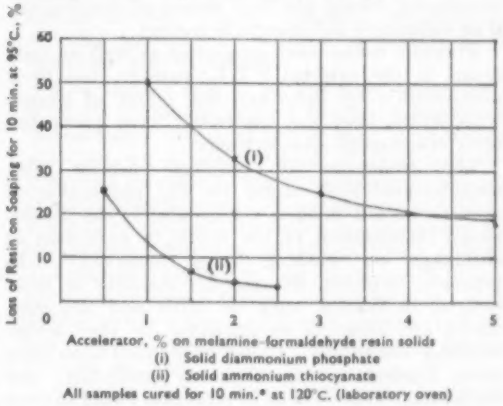


FIG. 4—Effect of Choice of Accelerator on Curing Rate of Melamine–Formaldehyde Resin

The possibility of migration of resin precondensates or dyes to the hot surface of the fabric during drying has considerable importance [21], and such migration of both resins and dyes has been patented for the production of fancy effects [22].

Ideal results may always be obtained in the laboratory by tensionless drying, and it should be emphasised that stretching of the fabric during drying also tends to cause surface resin deposition and should always be reduced to a minimum. It is clear, therefore, that suitable plant is an essential to the production of the best crease-resist finishes. Where the conditions are not ideal, it may still be possible to obtain reasonable results, provided that the method of processing is the best for the particular plant employed. After drying, the fabric is subjected to high-temperature baking in order to effect the final cure of the resin and render it fast to washing. This may be done by means of infrared units or by a hot air chamber, and the latter is more frequently employed for economic reasons, the normal baker being arranged so as to give a temperature of 140°C. and a passage of 3–4 min. Both shorter times at higher temperatures and longer times at lower temperatures have been advocated, but a treatment as outlined above would appear to represent the best compromise. In order to ensure that the fabric really attains the baking temperature, it should be baked immediately after drying and before moisture has been reabsorbed, or else it should be passed over a

predrier before entering the baker. After baking, the fabric should be washed off under alkaline conditions to remove free formaldehyde and by-products of the reaction. This washing-off process is sometimes omitted, and in such cases a fishy odour may develop immediately or during storage of the goods. This odour is said to be due to the production of methylamines and is particularly liable to occur where ammonium salt catalysts have been employed [23]. It may be reduced or prevented by addition of urea or dicyandiamide to the resin bath, but since these substances, particularly the former, may have a retarding effect on the cure of the resin, washing off is always to be preferred. Softening agents may also be introduced during the final stages of washing off, if an extremely soft handle is desired.

Phenolic resins were suggested as well as urea resins in the original T.B.L. patents, but their discoloration by light and the odour of phenol with which they are associated have prevented their commercial development.

The treatment of cellulosic fabrics with urea–formaldehyde resins for the production of crease-resistant finishes results also in the dimensional stabilisation of the fabric, a reduction in shrinkage on washing being observed [24]. In practice, however, dimensional stability is most desired in fabrics, such as drills and shirtings, which are liable to be subjected to very severe washing conditions. Under such conditions urea resin finishes are insufficiently wash-fast, and melamine resins [25] are to be preferred owing to their much greater resistance.

The method of application is similar to that outlined above, and again excessive stretching of the fabric during processing should be avoided. It is not possible to stretch a fabric excessively and stabilise it in this position by the use of resins, and if such a procedure is attempted the resultant finish is harsh and the dimensional stability unsatisfactory. The use of glyoxal–formaldehyde resins alone [26] or in conjunction with urea–formaldehyde [27] has also been advocated for stabilisation of cellulosic fabrics, and ethyleneurea resins [28] have also been used.

A factor to be considered in the laundering of resin-treated fabrics is their sensitivity to chlorine bleaches. Reaction of chlorine with the amino groups of the resin takes place and yellowing of the fabric occurs. This fixation of chlorine may be accompanied also by chemical tendering, particularly under the action of light, and much work has been done on this problem, chiefly in the U.S.A. [29], without a satisfactory solution being reached. It has been claimed that ethyleneurea resins are less susceptible to this defect, but the writer feels that this factor of chlorine sensitivity has been overemphasised, particularly in the U.S.A. It is undoubtedly true, however, that the use of chlorine bleaches on resin-treated fabrics should be avoided wherever possible.

2. PERMANENT GLAZED OR EMBOSSED FINISHES ON CELLULOSIC FABRICS

Resin processes used in the production of crease-resistant or dimensionally stable fabrics may also be used for the production of wash-fast mechanical finishes. The passage of the fabric through a glazing or embossing calender results in a deformation of the surface fibres, and this may be rendered permanent by resin treatment.

Earlier patents advocated urea–formaldehyde resins for this purpose [30], but subsequently the improved washing fastness obtained by the use of melamine resins has resulted in an increasing use of the latter [31] either alone or mixed with urea resins.

In the production of mechanical finishes of this type, the resin is applied to the fabric as before, and the fabric is glazed or embossed after drying and before baking. In this case, it is essential to minimise any precure of the resin before the glazing or embossing process, since this would confer a resistance to surface modification on the fabric. For this reason, drying should be adjusted so as to leave about 10% residual moisture in the fabric, and cooling of the fabric after drying (e.g. by passage over water-cooled cans) has been suggested [32]. Glazing or embossing should, for similar reasons, be carried out as soon as possible after application of the resin, and if the fabric has to be stored after drying, the batching of hot fabric or exposure to an acid atmosphere should be avoided.

Various modifications of the above process suggest themselves. For instance, the resin may be printed on the fabric to give a glazed or embossed pattern on a plain ground, or an alkaline printing paste may be used which will prevent cure of the resin on the printed portions of the fabric [33]. Permanently glazed or embossed pigment prints of good washing fastness may also be obtained.

The majority of permanent glazed or embossed effects have been produced on cotton fabrics, but much interest is at present being shown in the production of similar effects on viscose rayon staple fabrics. Such finishes are much more difficult to obtain in this case, and high degrees of permanent glaze or deeply embossed patterns are not usually produced commercially. It is suggested that this may be due to the partial cure of the resin which invariably takes place during drying. This will tend to produce a greater resistance to creasing and mechanical deformation in rayon than in cotton at this stage, and the fabric will thus tend to resist the glazing or embossing process. Resins of the ethyleneurea type have been suggested as giving superior results on spun rayons [34], and this may be due to a lesser tendency to precure. The difficulties may also be associated with the greater water sensitivity and swelling power of viscose rayon fibres.

An alternative type of process for the production of permanent glazed or embossed effects consists in the application of a surface film of resin which is itself glazed or embossed [35]. Processes of this type are not so extensively employed in industry, since surface coatings of resin invariably have a detrimental effect on the handle of the fabric, but interesting results are now being obtained commercially by the embossing of a surface coating of a thermoplastic resin such as polyvinyl chloride.

3. SHRINK-RESISTANT FINISHES ON WOOL

The felting shrinkage of wool due to the scaly structure of the fibres is entirely different from the shrinkage of cellulosic fabrics. The latter may best be compared with the relaxation or London shrinkage of wool fabrics. It is consequently surprising that resin processes should have been successful in the control of felting shrinkage. A number of resin treatments for this purpose have been proposed[36], however, and, although they have not been accepted commercially to any extent in this country, the reason is, not their failure to control shrinkage, but their effect on the handle of the wool.

For the prevention of swelling in cellulose, the resin should be formed as completely as possible within the cellulose fibres, and under these conditions the effect on the handle is minimised. In the case of wool, the control of felting obtained has been variously ascribed to masking of the scales of the wool fibre with resin, or to "spot-welding" of individual fibres to one another[37]. Regarding the former mechanism, the effect obtained would be due to an interference with the ratchet-like action of the scales similar to that obtained by their partial removal by chlorination processes. "Spot-welding", on the other hand, would tend to prevent the movement of the wool fibres in relation to one another, and reduce felting by this means. In either event, it is necessary for the resin to be on the surface of the fibres, and the handle of the wool is therefore affected to some extent. Both types of mechanism may well be involved in practice.

It has now been established that greater stiffening of wool fabrics will occur if resins of a low degree of polymerisation are employed, while, in addition, a greater quantity of resin must then be applied to achieve an adequate degree of shrink resistance. This would appear to be due to penetration of the wool fibres by low-condensed resin, which causes an internal stiffening of the fibres, but does not assist in any way in the prevention of felting.

Thus a melamine resin in a low state of condensation, though ideal for the treatment of cellulosic fabrics, will give an extremely stiff handle when applied to wool. A later process, consisting in the application of a colloidal solution of partly condensed resin[38], is found to improve matters, while a procedure in which the resin is boiled in acid solution in the presence of the wool, so that fully condensed resin is deposited on the fibres, is found to give even better results. In the latter case no stiffening is observed, but the surface deposition of resin, which is necessary to achieve the required resistance to felting, is found to impart a harshness of handle to the wool. In addition a dusting of resin from the dried fabric frequently occurs if larger quantities of resin have been employed. This external bonding of wool fibres has also been achieved by application of other types of polymers such as polymethyl methacrylate[39] or a nylon derivative[40], and here also a similar effect on the handle of the fabric has been observed. The so-called "melamine resin acid colloid" described above[38] may be cured by an acid boiling process instead of heat treatment, with a marked improvement in the handle of the treated wool.

It is probable that only a small quantity of resin in the right place on the fibre will give a satisfactory resistance to felting, and laboratory experiments have shown that sometimes as little as 0·5% resin on the weight of wool can give excellent results. It therefore appears that a large proportion of the resin employed does no useful work, but simply has an adverse effect on the handle of the wool. It is thought that the solution to the problem lies in this selective deposition of resin, and future developments may lead to a satisfactory process of this nature. The obvious advantage of resin treatments is that they are additive and not subtractive, and should therefore have economic advantages if suitably applied; the wearing properties of the fabric are also improved.

Two further aspects of the resin treatment of wool for shrinkage control should be mentioned. Considerably improved results may frequently be obtained by a pretreatment of the wool with hydrogen peroxide[41], while treatments of this type and a preliminary extraction of the wool with solvents have also been advocated in conjunction with the process based on solubilised nylon polymer. The peroxide treatment advocated is not in itself sufficient to impart resistance to felting, but would appear to affect the wool in such a way as to enable the resin to attach itself more readily to the required sites in the fibre.

A further effect observed is that the application of resin to the raw wool or to the yarn does not give as good a felting resistance to the final fabric as treatment of the fabric itself with the same quantity of resin. This would seem to be corroborative evidence for the "spot-welding" theory, since the mechanical operations of spinning and weaving would tend to break down any welding together of the fibres. In order to overcome this difficulty, treatment of the raw wool with the catalysed resin solution without any curing operation has been suggested[42]. The wool is then converted to fabric, and a baking treatment finally applied to cure the resin. Comparative shrinkage figures obtained after various melamine resin treatments of wool are shown in Fig. 5.

4. PERMANENT STIFFENED FINISHES

As previously explained, the application of urea–formaldehyde resins in a more advanced state of condensation than that required for crease-resist processes will have the effect of stiffening the fabric. Permanent stiffened effects are produced in this way, and the process may be cheapened by the use of resin–starch mixtures[43], the starch being insolubilised in the presence of the resin. A fall in tensile strength, tear strength, and abrasion resistance will be observed, but if a fabric of sufficiently high initial strength is chosen, satisfactory results are possible. Stiffening processes of this type should never be employed in conjunction with crease-resist finishes to give firmness of handle, since they are invariably detrimental to the degree of crease-recovery obtained and, particularly in the case of viscose rayon, the wearing properties of the

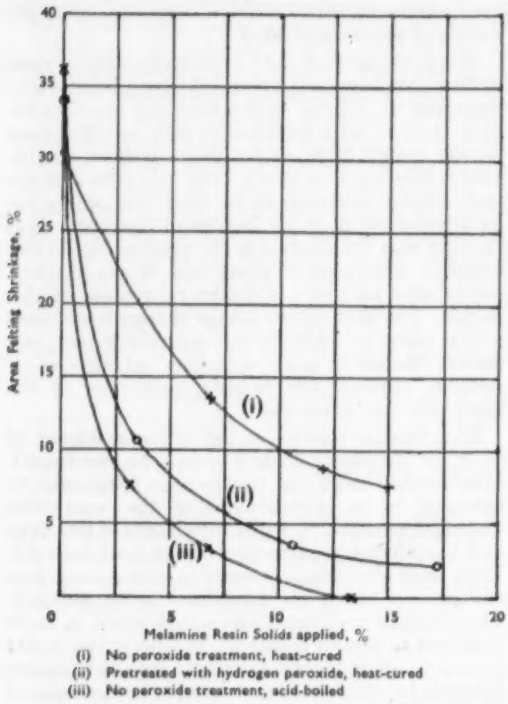


FIG. 5—Effect of "Melamine Resin Acid Colloid" on Felting Shrinkage of Wool Hosiery Fabric

fabric may be seriously affected [44]. A recent development is the use of special starch derivatives in conjunction with amino resins, and by this means considerable improvements in the strength and abrasion resistance of the treated fabric can be obtained [45].

An alternative method of stiffening fabrics is the application of polyvinyl resin emulsions, and polyvinyl acetate is frequently employed in this way. The polymerisation of the resin is complete before application to the fabric, and no curing treatment is therefore necessary. It has been observed, however, that the wash-fastness of the finish is much improved by thorough drying, which appears to prevent re-emulsification of the resin by soap solutions. Resins of this type do not lower the tensile strength of cellulosic fabrics and, furthermore, they increase the abrasion resistance as measured by recognised testing machines. It may be mentioned that abrasion resistance as measured by such machines is considerably lowered by urea- or melamine–formaldehyde resin treatments. This has given rise to doubts as to the wearing qualities of crease-resisted fabrics, but evidence has been advanced to suggest that such accelerated tests do not give results in accordance with practical wearing conditions, and under reduced loads resin-treated fabrics have been shown to be superior to the untreated materials [46].

The stiffening of wool fabrics and felts can also be achieved by polyvinyl resin treatment, but the quantity of resin applied should be relatively low to avoid dusting, and care should be taken that acidity of the wool does not cause precipitation of the resin in the padding bath.

5. IMPROVEMENT OF COLOUR FASTNESS

A large number of patents have been issued relating to the improvement of the washing fastness of direct dyes and the conferment of affinity for acid dyes [47] on cellulose. In practice, resins of the cyanamide- or dicyandiamide–formaldehyde type are preferred for this purpose, and they may be added to the spinning solution in the case of regenerated cellulose or applied before or after dyeing [48]. These resins are used in relatively low percentages and are extremely effective for their particular purpose, while similar results are obtained when crease-resist finishes are applied.

It has also been claimed that the light-fastness of direct dyes may be improved by resin treatments [49], but this is true only for a limited number of dyes, while others have their light-fastness reduced. It is therefore important to use selected dyes for resin processing, and provided that this is done a wide range of satisfactory colours is available [50]. Other dyes are found to be liable to undergo colour changes in the presence of formaldehyde, and their use must therefore be avoided.

A further application of resins which has resulted in a number of patents [51] is the conferment of resistance to gas fading on dyes for acetate rayon. Proposed methods of application include addition of melamine resin precondensates to the cellulose acetate spinning bath [52] and aftertreatment with resins of the dyed fabric [53].

6. PIGMENT PRINTING AND PADDING

The use of pigments in textile printing has always been considerable, but classical methods of fixing such colours by means of blood albumen, egg albumen, or casein have not given satisfactory fastness to washing or to dry and wet rubbing. The development of synthetic resins led to their examination for the purpose of pigment fixation, and a very large number of patents have resulted [54].

Water-soluble precondensates of urea- or melamine–formaldehyde resins have been advocated for this purpose [55], but early formulations were not very successful. Resin intermediates of this type are absorbed by the cellulose fibres, and little is left on the surface to act as an adhesive for pigment particles. Much greater progress was made by the use of solvent-soluble types of resin, usually in the form of emulsions. These resins are prepared by butylation of urea- or melamine–formaldehyde precondensates [56]. They are soluble in organic solvents such as xylene or Cellosolve, and were originally developed for the coating industry for use in the formulation of stoving enamels.

Resins of this type when applied to hard surfaces give brittle films which crack easily, and they are therefore employed in conjunction with alkyd resin plasticisers. Alkyd resins are essentially condensation products of polyhydric alcohols and dibasic organic acids, and are commonly based on glyceryl phthalate, whence their alternative name

of *glyptals* originates. They are modified for the purpose of formulating lacquers by the introduction of a proportion of long-chain fatty acid during the condensation, castor-oil fatty acid being most extensively used for this purpose. Alkyds may also be based on drying oils such as linseed oil, and in such cases they will harden at room temperature in the presence of suitable catalysts in the same way as ordinary linseed oil paints. The alkyd resins normally used in stoving enamel finishes are based on non-drying oils and invariably contain some free acid, which acts as a catalyst for the urea or melamine resins with which they are used.

Emulsions of such resin mixtures may be prepared and are successfully used in pigment printing [57]. The pigment may be ground into the resin, added to it as a paste in castor oil, or added to the final emulsion as an aqueous dispersion. The first of these methods gives the best rubbing fastness, but the use of aqueous pigment dispersions [58] will give satisfactory results for many purposes. The emulsions used may contain the resin either as the continuous [59] or as the disperse [60] phase and they may be cationic [61] or anionic [62] in nature. Recent developments have tended towards the production of a range of pigmented products which are simple to use and do not involve the addition of pigments by the textile printer [63].

The improvement in the results obtained in pigment printing and padding has been remarkable during recent years, and this may be partly attributed to the improved pigments of extremely small particle size which are now available. By the use of such pigments and addition to the printing paste of suitable thickeners to prevent absorption of the resin by cellulose, aqueous resin precondensates can now be employed to give prints of excellent rubbing and washing fastness.

7. MISCELLANEOUS RESIN APPLICATIONS

(*a*) *Showerproofing*

A number of patents have described the use of wax emulsion showerproofing compositions in conjunction with crease-resist resins for the production of combined showerproof and crease-resistant finishes [64]. Unfortunately, however, the resin has no effect on the resistance of the wax emulsion finish to washing or dry-cleaning. The development of Velan PF (ICI) for wash-fast showerproofing led to patents for its use in conjunction with crease-resist finishes [65], while it may also be included in the resin bath [66].

A further development in this field has led to many patents [67] based on stearamide or methylolstearamide in conjunction with amino resins, and products of this type are now commercially available and enable combined crease-resist and showerproof finishes to be applied from a single bath. A recent patent [68] has suggested the use of silicones in conjunction with crease-resist resins in the same way, and excellent results can be obtained in this manner.

(*b*) *Flameproofing*

The production of flameproof textile fabrics which retain their fire-resistance on washing has aroused considerable interest, particularly for military purposes, and in this field also, formulations based on amino resins have been suggested. These have usually been based on the fixation of inorganic flameproofing materials by means of amino resins, and tungsten [69] and antimony [70] compounds in conjunction with resins have both been recommended in the patent literature. Other processes are based on the use of phosphates in association with urea [71], melamine [72], or cyanamide resins [73], such methods being easier to apply commercially.

The fundamental problem with such finishes is that the quantity of resin required to bind sufficient phosphate to the fabric is very high, 20–30% resin solids on the weight of fabric being commonly employed. Such large amounts of resin have an undesirable effect on the handle of the fabric; they are also liable to cause embrittlement and excessive loss of tensile strength. In addition, although the finishes obtained are fast to mild washing, they are not comparable in durability with other types of resin finish. A more recent development is the use of THPC (tetrakishydroxymethylphosphonium chloride) in conjunction with melamine resins, for which excellent wash-fastness is claimed [74].

A resin based on thiourea has also been advocated for reducing the inflammability of nylon [75].

(*c*) *Stabilisation of Lace and Net*

The shrinkage and the distortion of lace and net which occur on washing can be substantially eliminated by treatment with mixtures of melamine–formaldehyde precondensates and polyvinyl resin emulsions [76]. The former prevent swelling of the cellulose and control shrinkage, while the latter impart a permanent crispness to the material and prevent distortion during washing. The proportions of the two components may be varied according to the firmness of the handle required, and various polyvinyl resins may be employed, the principal being polyvinyl acetate and polymethyl methacrylate.

(*d*) *Stiffening of Synthetic-fibre Fabrics*

Synthetic fibres such as nylon and Terylene are not permeable to resin solutions; all types of amino-resin precondensates are deposited on the surface and result in stiffening of the fabric. Substantial quantities of nylon dress net are treated with melamine resins in order to impart a permanent firmness of handle, while heavy nylon mesh shoe fabrics, which require to be extremely stiff, are processed with higher concentrations of a similar product. A recent patent has disclosed the use of amino resins for preventing the entrainment of water by synthetic-fibre fabrics [77], nylon, Orlon, and Terylene being mentioned in particular.

It should be pointed out that, owing to the presence of –CO·NH– groups in the nylon molecule, amino resins appear to be more firmly bonded to nylon than to other fibres. This may cause some difficulty in stripping off the resin finish if this should be necessary. Cellulose acetate and Terylene fabrics are stiffened in a similar manner, and wash-fast finishes may be obtained. The situation of the resin on the surface of the fibres renders it more

susceptible to removal in washing; for this reason, melamine resins are to be preferred in such applications.

* * *

The main advantages conferred by plastics on textile fabrics have been outlined above, but development in this field is taking place continuously, and it is therefore impossible to come to any final conclusion as to the future relationship between the textile and the plastics industries. It remains to suggest that close co-operation between the two industries is essential to future development in a field such as this, where each has much to learn from the other.

I should like to thank my colleague, Mr. A. Bennett, and also Dr. T. F. Cooke and Mr. P. B. Roth of the American Cyanamid Co., for helpful criticism of this paper. Thanks are due also to the Directors of British Industrial Plastics Ltd. for permission to publish.

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Gy, *BP* 576,562, 588,990;
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COMMUNICATIONS

A Study of Certain Natural Dyes
I—The Adsorption of Brazilwood and Logwood Colouring Matters by Fibres

F. M. ARSHID, J. N. DESAI, D. J. DUFF, C. H. GILES, S. K. JAIN, and I. R. MACNEAL

The adsorption properties of hæmatein, the colouring matter from logwood, and its leuco compound, hæmatoxylin, together with brazilein, the colouring matter from brazilwood, have been studied on several types of fibre. Brazilein and hæmatein are weak acids and are adsorbed by wool or nylon appreciably only from acid solutions, probably by hydrogen bonding between the fibre and the undissociated hæmatein or brazilein molecules, as well as by acid–base combination with the charged amino groups in the fibre. Very high adsorption values observed at about pH 1·0 may be indicative of some hydrolytic breakdown of the fibre. In solutions less acid than about pH 7 adsorption is very low on account of the mutual repulsion between the colouring matter anions and the negatively charged fibre.

Hæmatoxylin is a tetrahydric phenol and has the very unusual property, in a single substance, of appreciable substantivity for cellulose as well as for cellulose acetate, nylon, and protein fibres. A study of the apparent heat of adsorption, of the nature of the isotherms, and of the affinities leads to the conclusion that its adsorption by cellulose acetate, nylon, and wool is most probably attributable to the formation of hydrogen bonds with the fibre, those formed by nylon and wool being stronger than those formed by cellulose acetate.

The adsorption by cellulose, studied by the same means, appears to be of a different nature and to be attributable to weaker forces, probably van der Waals attraction. Since hæmatoxylin, with four strong hydrogen-bonding groups, does not seem to form hydrogen bonds with cellulose in water, it is unlikely that any dyes can do so, and their adsorption may therefore be due to physical attraction and not to hydrogen bonding.

Some evidence is given that hæmatoxylin may act as a cross-linking agent between the peptide groups in the molecular chains of proteins.

Analytical methods for the colouring matters are evaluated. Refractometry was used in determining the adsorption of hæmatoxylin. A simple and effective method of packing loose fibres for adsorption tests is described.

Introduction

The investigations made in recent years upon the theoretical basis of dyeing mechanisms have been concerned with synthetic dyes, usually sulphonated azo dyes. Little or no attention has been paid to the use of natural colouring matters. Scientific research has thus reflected the prevailing technical practice, for the natural products are now of much less importance than the synthetic dyes. Nevertheless, a study of the dyeing processes of the natural materials should have some intrinsic interest, because the structural features responsible for their colour and dyeing properties differ markedly, in most cases, from those of their synthetic counterparts.

A systematic investigation has therefore been undertaken to elucidate the details of the processes by which logwood black, in particular, is formed in the fibre. This natural colouring matter is still widely used and, moreover, its molecular structure bears some resemblance to that of natural tannins, so that its reactions with protein fibres and metals may have interest in other directions.

The history and the properties of the material have been admirably summarised by Bird and Newsome [4], who made very thorough investigations to establish the dyeing and mordanting methods necessary for obtaining the best fastness properties. Logwood is the heartwood of the tree *Hæmatoxylon campechianum*, grown mainly in the West Indies. Introduced into Europe by the Spanish after their American conquests, its use became so well established that by the middle of the nineteenth century it had become the most important of all dyes; but with the increasing use of synthetic products, often of superior fastness properties, its importance has declined, though it is still in quite widespread use, and indeed is the only natural colouring matter which is now consumed in large quantities.

When dyed with a chromium mordant, logwood produces a black with an attractive bluish cast, and it can be used on wool, silk, leather, nylon, and acetate rayon. Aluminium, copper, iron, and tin were used as mordants in earlier times, but chromium is almost exclusively used today, except for silk, for which iron and tin (stannic) are preferred. The colouring principle of logwood is hæmatoxylin (I*a*) (*C.I.* 1246), which is itself colourless, but is readily oxidised to the dark brown hæmatein (I*b*).

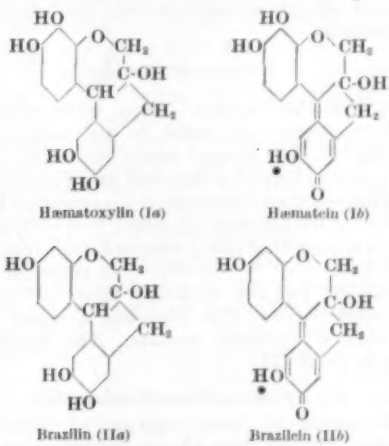
The woods of various kinds of *Cæsalpinia* tree, e.g. Brazil wood and Lima wood, also yield corresponding colouring matters closely related in structure, viz. brazilin (II*a*) and brazilein (II*b*) (*C.I.* 1243). The brazilwood colouring matters dyed on a chromium mordant produce reddish purples to browns of indifferent fastness properties and of little current importance.

The structures of all these compounds were first determined by W. H. Perkin Jr. and Robinson and their collaborators in their classical researches made between 1900 and 1910[10,12,18,19], though the compounds have never been synthesised.

COMMERCIAL LOGWOOD PRODUCTS

As a preliminary to the main research, analytical methods for the colouring matters, in both com-

mercial and purified forms, were investigated. The commercial brands of logwood—Hematine or Logwood Crystals—are prepared by evaporation of aqueous extracts of the wood. They contain both hæmatoxylin and hæmatein, the proportions varying from one brand to another according to the degree of oxidative treatment given during manufacture, and consist of dark brown shiny flakes containing considerable quantities of impurities, apparently tannins, resinous matters, and carbohydrates. When wool is immersed for a short period in a cold solution of these products, a blue–grey compound which fades rapidly in air or on acidification is first absorbed. Chromatographic analysis of the "100% oxidised" material on silica powder gives three broad bands: the lowest contains a bluish material, giving a reaction for tannins, while the middle and largest band appears to consist of hæmatein. Volumetric and spectrographic methods of analysis of these materials were employed, but an established technical method of evaluation is by trial dyeing on oxidised and reduced chrome mordants. This was found to give closely similar results to the more precise quantitative methods (see Table I). The trial dyeing method is therefore quite reliable in determining the hæmatein content of commercial samples.



It was found that hæmatein suffers some decomposition during the normal dyeing process. This is believed to be due to oxidation of the reduced ring system of the molecule, which, being attached directly to an aromatic ring, is made more susceptible to oxidation (see Part II).

DETERMINATION OF THE ADSORPTION OF HÆMATOXYLIN BY FIBRES AND ITS RELATION TO DYEING MECHANISMS

In this work the adsorption of hæmatoxylin by various substrates from aqueous liquors has been determined by analysis of solutions before and after application. For reasons described more fully in the Experimental section (p. 400) the analyses suffer from errors, due partly to the unavoidable oxidation of a small proportion (ca. 5%) of the reagent during the tests and to other unidentified causes. Cellulose and cellulose acetate give more reproducible results than nylon and wool, which appear to be more active in promoting oxidation. The presence of reducing agents does little to improve matters, though hydroxylamine sulphate was used in some tests. It appeared to have little effect on the adsorption by wool (Fig. 1) but to increase the affinity for nylon considerably (Fig. 2); this may be due to a swelling action on this fibre. In order, therefore, to obtain satisfactory mean results, the tests were repeated many times. It will be seen that the typical isotherms shown for nylon and wool are not determinable with any high

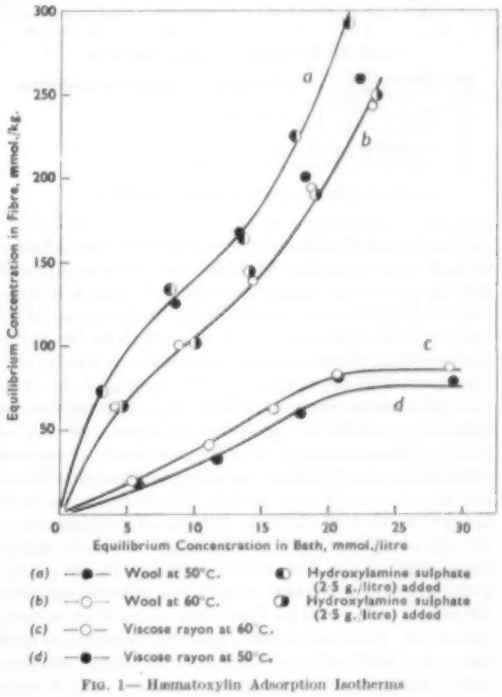

Equilibrium Concentration in Fibre, mmol./kg.
Equilibrium Concentration in Bath, mmol./litre
(a) Wool at 50°C.
(b) Wool at 60°C.
(c) Viscose rayon at 60°C.
(d) Viscose rayon at 50°C.
Hydroxylamine sulphate (2·5 g./litre) added
Hydroxylamine sulphate (2·5 g./litre) added

FIG. 1—Hæmatoxylin Adsorption Isotherms

TABLE I

Composition (%) of Brands of Hematine Crystals

	Hæmatoxylin (by $K_2Cr_2O_7$)	Hæmatein, by— Spectroscopy	Hæmatein, by— $TiCl_3$	Trial Dyeing
Hematine Crystals NAD, 15% oxidised...	38	10·0	20*	10–12·5
Hematine Crystals M, 50–60% oxidised...	24	15·1	35*	15–20
Hematine Crystals ZA, 100% oxidised ...	0·5	30·1	60*	25–30
Pure crystalline hæmatein (99·7%) ...	—	100·0	99·5	(100)

*The high values can be accounted for by the method having returned impurities as well as hæmatein.

precision, but a reasonable estimate of the apparent heats of adsorption can be made from them (see below).

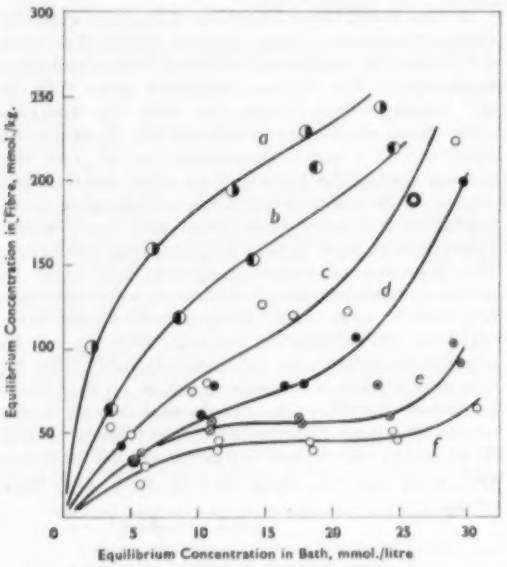

Equilibrium Concentration in Fibre, mmol./kg.
Equilibrium Concentration in Bath, mmol./litre
(a) Nylon at 50°C. } Hydroxylamine sulphate (2·5 g./litre) added
(b) Nylon at 60°C. }
(c) Nylon at 50°C. } No addition
(d) Nylon at 60°C. }
(e) Cellulose triacetate at 50° C. } No addition
(f) Cellulose triacetate at 60° C. }

FIG. 2.—Hæmatoxylin Adsorption Isotherms

The forces which are responsible for the adsorption of dyes by fibres are believed to be comprised largely of (*a*) ionic attraction, (*b*) hydrogen bonding, and (*c*) physical or van der Waals attraction: (*a*) is concerned in the adsorption of acid dyes by nylon and protein fibres, and its operation is fairly well understood [22]; (*b*) and/or (*c*) [23,24] may also be concerned in these cases; while dyeing on cellulose and cellulose acetate is probably a result of (*b*) or (*c*) [1,23]. The operation of the non-ionic forms of attraction, viz. hydrogen bonding and van der Waals attraction, in dyeing is not, however, so clearly defined as that of the ionic forces. Hæmatoxylin is an especially useful material with which to study these attractions, because it exhibits the property, very unusual in a single substance, of substantivity for cellulose as well as for cellulose acetate, nylon, and wool. It has also four (phenolic) groups, which are potentially strong hydrogen-bonding centres, and a fairly large and planar molecule, which may exhibit appreciable van der Waals attraction for the fibrous substrates.

The differences between the nature of the adsorption by the various fibres have been examined in this work by three procedures—(*a*) affinity studies, (*b*) measurement of apparent heat of adsorption, and (*c*) examination of the shape of the isotherms.

(*a*) *Affinity Studies*

It was thought that the use of a more efficient solvent than water might reduce the affinity for the various fibres sufficiently to emphasise any differences. Ethanol–water (50 : 50) was found to be suitable for this purpose, and a few tests were made with it. The adsorption by all the fibres from this solvent is found to be much lower than it is from water (Table II), but it is still appreciable and well within the measurable limits in the case of cellulose acetate, nylon, and wool. Cellulose, however, loses all its adsorptive power.

TABLE II

Adsorption of Hæmatoxylin from 50% Aqueous Ethanol

C_B = Equilibrium bath concn. (mmol./litre)
C_F = Equilibrium concn. in fibre (mmol./kg.)
Temp. 60°C.; time 24 hr.; 0·5 g. fibre in 10 c.c. soln.

Fibre	C_B	C_F
Cellulose (viscose rayon) ...	6·7–26·5	Nil
Cellulose triacetate	1·0	ca. 1·0
	2·5	25
Nylon	0·9	40
	2·5	40
Wool*	0·9	45
	2·0	33
	2·6	25

*The *fall* in adsorption by wool with *increase* in bath concentration is an effect attributable to association in the solvent [7].

Direct affinity calculations were also made using the formula—

$$-\Delta\mu = RT \ln \frac{C_F}{VC_B}$$

where V is the "volume" term, representing the effective volume of water in the substrate (in litres/kg.) [23]. For viscose rayon the value of 0·45 for V, as employed by Marshall and Peters [17], was used; for cellulose triacetate 0·1, as used by Fowler and Michie for cellulose diacetate [22 at p.276], though it is not certain that this is correct for the triacetate; and 0·3 for wool [cf. 22 (p.296)]. No value for nylon is available, but the arbitrary figure of 0·05 has been used because this fibre has a regain about half that of cellulose acetate. The results are given in Table III.

(*b*) *Apparent Heats of Adsorption*

The apparent heat change of adsorption measured directly from the isotherms is the result of two successive operations—(i) the removal of solute from the solvent and (ii) its attachment to the substrate. It is not therefore a direct measure of the strength of the solute–substrate bond, but it can be used to give a comparative measure of this bond for a series of different substrates if both solvent and solute are the same throughout, as they are in this case.

The apparent heats of adsorption for hæmatoxylin are shown in Table III. They may be compared with the values for phenol, from water, on cellulose triacetate [6], on nylon [7,15], and on wool [7], which are −3·0, −4·5, and −4·0 kcal./mole respectively.

(*c*) *Nature of the Isotherms*

The isotherms for cellulose are S-shaped (Brunauer type V), in contrast to those for the other three substrates, which may be classed as "Brunauer

type II", being concave to the x-axis in the lower region. These differences in shape probably reflect a lower affinity of hæmatoxylin for cellulose than for the other three substrates [13].

TABLE III

Apparent Heats of Adsorption and Affinities of Hæmatoxylin

Substrate	C_F (mmol./kg.)	ΔH_a (kcal./mol.) (50–60°C.)	$\Delta\mu$ (kcal./mol.) (60°C.)
Viscose rayon	25	−3·5	−1·25
	50	−3	−1·3
	70	−2·5	—
Cellulose triacetate ...	25	−7·5	−2·6
	35	−7·5	−2·6
Nylon*	25	(−10)	−3·3
	45	—	−3·3
	60	(−10)	—
Wool	25	—	−2·7
	50	−11	—
	100	−11	−2·4
	150	−8	—

* No addition to bath

Nature of Bonds with Cellulose, Nylon, and Wool

The consistent conclusion of all these tests appears to be that in both strength of bond and affinity the fibres may be placed in the order—nylon and wool > cellulose acetate > cellulose—and when other relevant facts e.g. [1,7,16,27] are taken into consideration, the most likely interpretation of this order is that cellulose adsorbs by physical attraction, and the other materials by hydrogen bonding, the cellulose acetate hydrogen bond being weaker than those of nylon and wool.

Reference to the regression line of the affinity values for cellulose of a series of aminoanthraquinone vat dyes on their molecular weight, given by Vickerstaff [24, Fig. 3], shows that the value obtained here for hæmatoxylin (mol. wt. 302; affinity −1·25 kcal./mol.) falls almost exactly on this line. Vickerstaff states that in the case of these and other vat dyes the affinity for cellulose must be largely attributable to van der Waals forces proportional to the molecular area, and the conformity of hæmatoxylin with the same relation further strengthens the belief that its affinity also arises from the same cause.

If cellulose cannot form hydrogen bonds in water with a compound like hæmatoxylin, which has so many powerful hydrogen-bonding centres, it seems unlikely that it can do so with any normal dyes.

Nature of Bond with Cellulose Acetate

Bonds between hydroxylic solutes and nylon or wool are believed to be largely of O...H...O type [7], involving the hydroxy group of the enolic form of the amide or peptide linkages in these fibres. It has been suggested [16] that phenol also forms O...H...O bonds with the carbonyl oxygen atom of the acetyl group in cellulose acetate. A similar mechanism may also operate in the present case, but it does not necessarily follow that the non-ionic compounds used as dyes for cellulose acetate, i.e. the disperse dyes, dye entirely by the same mechanism. These are almost insoluble in water and are believed to dye from a saturated but very weak solution of dye in the aqueous phase, which is maintained saturated by the presence of solid dispersed dye [3,5,23,25]. Even so, some initial attraction between dye and substrate must be necessary. This may be O...H...O hydrogen bonding in some cases, but not in all, because a number of disperse dyes have no hydrogen atom free to form such a bond. In their case another form of bond, e.g. a C...H...O or C...H...N bond [1] or van der Waals attraction, may be operating.

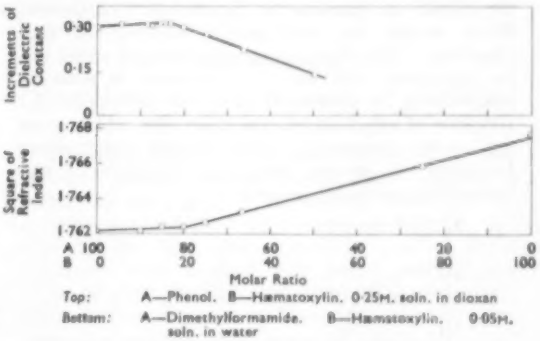


FIG. 3—Complex Formation in Binary Solutions

Cross-linking of Wool by Hæmatoxylin

All four phenolic groups in hæmatoxylin appear to be able to combine simultaneously, by hydrogen bonding, with molecules of phenol or a water-soluble amide, because evidence is obtained of a 1 : 5 complex with phenol (in dioxan, by dielectric constant measurement cf. [14]; the fifth phenol molecule is presumably attached to the alcoholic group) and of a 1 : 4 complex with dimethylformamide (in water, by refractive index measurement) (Fig. 3). If four amide groups can thus be linked together by one molecule of hæmatoxylin, this compound may act as a cross-linking agent for wool by combination with sets of peptide linkages in the fibre. If so, corresponding changes would be expected in load–extension diagrams of treated wool fibres. It would be expected that both the tensile strength and the extension at break would be increased when hæmatoxylin is adsorbed—the tensile strength because the new hydrogen bonds between the solute and the peptide groups in the fibre, being as they are phenolic in character, should be stronger than the purely aliphatic interchain bonds which they replace; and the extension because the cross-links formed by hæmatoxylin are considerably longer than those between adjacent peptide groups, which they replace. This will ensure greater longitudinal freedom of movement, just as the lengthening of the cross-links in a set of parallel rules would do*.

* This would apply whether the protein molecules of the fibre are arranged parallel to the fibre length or are present as corpuscles, as recently suggested by Wormell [28].

A few load–extension tests were therefore made on wool fibres containing adsorbed hæmatoxylin in a state of equilibrium with the adsorption liquid, and on some fibres which had been treated with phenol, in comparison with untreated wet wool fibres. The measurements are not sufficient in number for any precise quantitative conclusions to be drawn, but the trend is very clear. The results (Table IV) show very definite increases in both extensibility and strength after treatment with the solute, and so confirm the predictions, though they cannot be considered firm proof of a cross-linking mechanism because phenol behaves similarly. Phenol, of course, being a monofunctional hydrogen-bonding compound, cannot act as a cross-linking agent, but it can break interchain bonds in the fibre. An increase in extensibility of treated fibres would be anticipated, and is in fact observed. The effect on tensile strength could not be predicted, but since an increase is actually observed it is presumed that the intermolecular cohesion of adjacent phenol molecules, which must act as the restraining force against longitudinal breakage, is greater than the strength of the cross-links normally present.

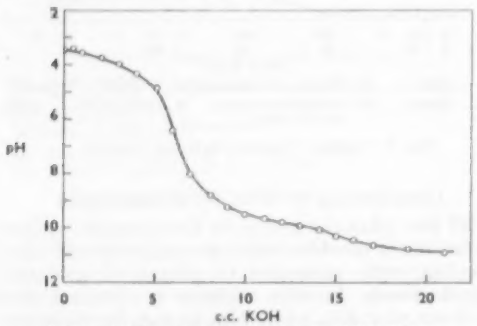


FIG. 4— Electrometric Titration Curve of Hæmatein

Swelling Action

The ability of hæmatoxylin to combine with each of the groups which are most abundant in cellulose acetate, nylon, and wool, together with the fact that its operative centres have high affinity for these, will probably cause it to act as a powerful swelling agent for the fibres. This appears to be so, for the isotherms (Fig. 1–2), after attaining a first maximum, commence to rise again steeply.

Effect of pH

The molecule of hæmatoxylin is non-ionic, and so, being uncharged, its adsorption should be uninfluenced by the charge on the fibre. To confirm that this is so, determinations were made from solutions of constant concentration but of differing pH values. The adsorption is almost independent of the acidity* (Fig. 5 (*c*)) and is markedly different in this respect from that of hæmatein, which is discussed below.

Brazilin

Owing to the very small quantity of brazilin available no adsorption experiments were made with it, but there seems no reason to doubt that it would be adsorbed very similarly to hæmatoxylin.

Use of Tetramethylhæmatoxylin

An attempt was made to measure the adsorption of this compound by viscose rayon. It is insoluble in water and was applied from 50% aqueous ethanol solution at 60°C. in initial concentrations ranging from 5·5 to 22 mmol./litre. No adsorption could be detected.

VALUE OF PHENOLIC COMPOUNDS AS COLOURING MATTERS

On account of its phenolic nature and the consequent high affinity of hæmatoxylin for the principal groups in the molecular structure of cellulose acetate, nylon, and wool, it can readily be adsorbed from neutral dyebaths in amounts large enough to ensure the formation of deep blacks when a metallic mordant is applied. This suggests that polyhydric phenolic compounds as a class might be examined with a view to the discovery of new non-ionic dyes with high affinity for these fibres.

ADSORPTION OF HÆMATEIN AND BRAZILEIN

These each have a phenolic group activated by an *ortho*-quinone group, and so they have weakly acidic properties, which are in fact intermediate between those of phenols and carboxylic acids, the pK_a value for hæmatein being 6·5 and pK_b 10·3 (Fig. 4)†. Its water solubility is too low for pH adjustment of its solutions to be varied over more

* A very slight rise with increase in acidity (too small to be shown in Fig. 5 (*c*)) is actually noticed, perhaps caused by increased fibre swelling.

† Cf. pK for simple unsubstituted aliphatic and aromatic carboxylic acids, ca. 4·75–5 (acetic acid 4·75) and 9·5 respectively; and for monohydric phenols 8–10. Catechol has $pK_b = 9·4$.

TABLE IV

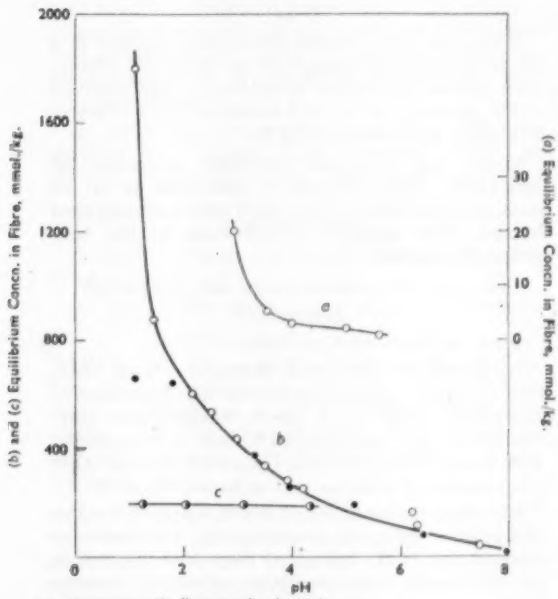
Mechanical Characteristics of Treated and Untreated Single Wool Fibres

(20°C. and 65% R.H.)

(Original fibre length 50·5 mm. Rate of loading 43·5 g./min.)

UNTREATED									Mean
Breaking load, g.	12·7	9·8	14·2	11·9	11·3	12·7			12·1
Extension at break, % ...	17	12	10	8	6	6			9·8
TREATED WITH PHENOL									
Breaking load, g.	19·8	18·4	17·0	22·5	14·2	18·4	19·8		18·6
Extension at break, % ...	30	25	20	30	22	22	26		25
TREATED WITH HÆMATOXYLIN									
Breaking load, g.	24·0	25·5	31·0	28·4	24·0	25·5			26·4
Extension at break, % ...	34	31	37	37	26	28			32·2

than a very limited range, and only a small portion of a direct titration curve with wool (Fig. 5 (*a*)) can thus be plotted. By adjusting the pH value with added mineral acid, however, a titration curve is obtained for nylon or wool with hæmatein or brazilein showing the expected characteristics (Fig. 5 (*b*), 6). Hæmatein anions are unable to penetrate the fibre against its normal negative charge, and on the alkaline side of pH 7 the molecule is almost entirely dissociated, so that the fibre does not adsorb hæmatein appreciably under these conditions. As the pH is reduced, however, the increasing extent of charge on the amino groups of the fibre attracts hæmatein anions from the bath up to the limit (ca. 850 mmol./kg.) of the free amino groups present, more hæmatein molecules in the bath becoming dissociated to maintain the equilibrium therein. Simultaneously an additional quantity of hæmatein is adsorbed in the undissociated state, largely by hydrogen bonding, so that the total amount taken up rises eventually above the figure corresponding to the free amino groups. This is a similar behaviour to that found for other weak acids by Steinhardt *et al.*[22].



(*a*) Hæmatein, pH adjustment by change in concn. 1·0–0·1 g./litre, 60°C., 12 hr.

(*b*) Hæmatein (○) and Brazilein (●), pH adjustment by mineral acid addition 2·0 g./litre, 85°C., 8 hr.

(*c*) Hæmatoxylin, pH adjustment by acid addition 8·0 g./litre, 60°C., 12 hr.

FIG. 5—Adsorption of Hæmatoxylin, Hæmatein, and Brazilein by Wool under Various Conditions of Acidity

The very high adsorption at the lowest pH value is probably partly due to some hydrolytic breakdown of the fibre under the severe experimental conditions, which will lead to the formation of additional amino groups in the fibre. Steinhardt *et al.*[22] consider prolonged adsorption tests at such low pH values to be unreliable for this and other reasons.

Conclusions

The general conclusions of this work may be summarised thus—

(*a*) Hæmatein and brazilein, being weak acids, are adsorbed by nylon and wool both as undissociated molecules, most probably by hydrogen bonding, and as anions, by electrovalencies.

(*b*) Hæmatoxylin (and probably brazilin also) is adsorbed by strong hydrogen bonds on nylon and wool and by weak hydrogen bonds on cellulose acetate. All four of the phenolic groups in its molecule may be active in adsorption, and it appears to act as a cross-linking agent for the fibres*.

(*c*) Hæmatoxylin is adsorbed on cellulose probably by van der Waals attraction and not by hydrogen bonding.

Experimental

PREPARATION AND PURIFICATION OF MATERIALS

Hæmatoxylin

The commercial pure product (100 g.), a buff-coloured powder, was dissolved in 500 c.c. of boiling water containing a little sulphur dioxide; the solution was clarified with charcoal, filtered, and cooled. The long thin colourless needles which separated were washed with water containing a little sulphur dioxide and dried in a desiccator. The product separating from concentrated solutions is a monohydrate, the stable form in air; on rapid heating this loses water and melts at 140°C. Slow heating produces an anhydrous form, m.p. 240°C. (decomp.). From dilute aqueous solutions a trihydrate separates, m.p. ca. 100°C. (depending on rate of heating). This slowly changes to the monohydrate on keeping.

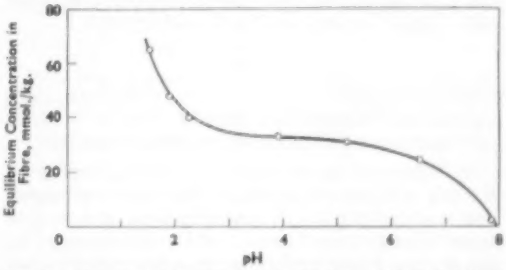


FIG. 6—Adsorption of Hæmatein by Nylon from Acidified Solutions 1 g. fibre, 400 c.c. liquor (initial concn. 1 g./litre), 85°C., 18 hr.

Hæmatein

Pure commercial hæmatoxylin (100 g.) was dissolved in 1250 c.c. of hot water, 125 c.c. of ethanol was added, and the solution cooled; 140 c.c. of sodium hydroxide solution (400 g./litre) was then added, with stirring and cooling to below 25°C., followed by gradual addition of 37 c.c. of aqueous hydrogen peroxide (100 vol.) diluted to 50 c.c. After 5 min. the solution was neutralised with dilute hydrochloric acid (10%) and acidified with dilute acetic acid (25%). An amorphous brown precipitate of hæmatein settled out, which

* Cellulose acetate dyed with logwood black is insoluble in acetone. Presumably cross-links are present between the fibre and the phenolic groups of hæmatein not involved in lake formation (see Part II).

was filtered, washed with water, and then gently warmed on a water-bath in 700 c.c. of water, whereby it was changed into the crystalline form. The crystals were filtered off, washed with methanol, and dried. Yield, about 70%.

Several other preparative methods were also used, but all gave low yields. They included oxidation of alkaline solutions of extracts of logwood chips or of pure hæmatoxylin by air bubbling for >6 hr., and recrystallisation of dried commercial "red hæmatein paste" from ethanol, after addition of ether to remove tarry matter.

Hæmatein forms minute red-brown platelets, with a greenish lustre (m.p. 210–216°C. (decomp.)). It is sparingly soluble in hot water (2·1 g./litre at 60°C.). Care must be taken to avoid prolonged heating when dissolving this compound in water, owing to the danger of oxidative decomposition.

Brazilin

A mixture of 100 g. "Brazil Wood Extract O" powder, 200 c.c. water, and 25 c.c. sodium bisulphite solution (25% SO_2) was heated on the water-bath until solution was complete, and then diluted with water to 400 c.c. The liquid was next transferred to a continuous ether-extraction apparatus and extracted for several consecutive days with fresh ether, the extract being withdrawn each day, the whole finally evaporated to dryness, and the residue recrystallised first from acetone and then from water. The yield is small because much of the product is retained by resinous matter and cannot be crystallised.

Brazilin forms colourless leaflets (changing to a pale cream colour in air) of monohydrate, m.p. 175°C. (The *Colour Index* mentions also a hydrate with $1\frac{1}{2}H_2O$, giving needle-shaped crystals.)

Brazilein

Two preparative methods were tried, both using commercial "Unoxidised Brazilin Powder" (which gave better yields than the "oxidised" material)—

(i) 100 g. of the powder was well mixed with 200 c.c. cold water and allowed to stand overnight. The supernatant liquor was decanted, the residue again treated with 200 c.c. cold water, allowed to stand a few hours and again decanted, then mixed with a further 100 c.c. of cold water, separated by filtration on wool, washed with a little ethanol but not dried, and recrystallised from methanol.

(ii) The crude powder was dissolved in boiling aqueous ethanol, clarified with charcoal, and the solution filtered and cooled. Ether was then added to precipitate tarry matter, the upper layer was decanted off and concentrated until an impure crystalline product separated, this being collected and dried. Ten grams of the solid was suspended in glacial acetic acid (90 c.c.), hydrogen peroxide (15 c.c. of 30% soln.) was added, and the mixture warmed to 30–40°C. until solution was complete (ca. 1 hr.). The temperature was then raised to 50°C. and the liquid allowed to cool overnight. The crystals which separated were collected and recrystallised from glacial acetic acid.

Brazilein forms minute dark brown crystals with a metallic lustre; it does not melt below 360°C.

Tetramethylhæmatoxylin

This was prepared by the action of excess of dimethyl sulphate and alkali on hæmatoxylin. Minute rod-like colourless crystals, m.p. 138°C.

Cellulose Acetate

Powdered cellulose triacetate (acetyl value as acetic acid 62·2%) was used.

Nylon

Bright drawn yarn (15 filament, 45 denier) was scoured in a 0·5% solution of a non-ionic detergent (Lissapol N) (ICI) with addition of a little ammonia, at 60°C. for 15 min., then well rinsed in distilled water.

Viscose Rayon

Spun rayon fabric was used, having the following specification— fibre length 6 in., fibre denier 6, approx. 200 fibres in the cross-section of each yarn, ends 30 per in., picks 25 per in., warp and weft 1/12s linen count, weight 9–10 oz./sq.yd.

Wool

Root ends of a Lincoln fleece were scoured in a dilute solution of Lissapol N at 60°C. for 5 min., then rinsed first in hot and then in cold distilled water, dried at 95°C., and extracted with ether in a Soxhlet apparatus for 24 hr.

Before use all fibres were first oven-dried at 100–110°C., then allowed to condition in air at room temperature for 24 hr., and stored in stoppered bottles. The weights quoted refer to the conditioned material.

ANALYSIS OF HÆMATOXYLIN AND HÆMATEIN

*Hæmatein**

Four methods were examined—

(i) TITANOUS CHLORIDE METHOD—Back titration was used with electrometric determination of end-point. This gave good results with pure hæmatein, but much higher values than expected with commercial products, because it returns other components of these as well as hæmatein itself.

(ii) SPECTROGRAPHIC ANALYSIS—Solutions (0·1 g./litre) of pure hæmatein in Cellosolve or ethanol, and of the brands of Hematine Crystals in distilled water, were employed, ultraviolet spectra being recorded on a photographic plate using a spark discharge between tungsten steel electrodes. The wavelength 2800 A. was used for quantitative analysis.

(iii) TRIAL DYEING—This is an accepted technical procedure and it was used in order to assess its true value in determining hæmatein content. Two hanks of wool were mordanted with "reduced chrome" mordant (3% potassium dichromate + 6% tartaric acid, on weight of fibre) and "oxidised chrome" mordant (3% potassium dichromate + 3% sulphuric acid) respectively, and

* Rawson and Trimble in 1885 [31] colorimetrically analysed alcoholic solutions of aluminium and copper lakes of hæmatein. Few details are given. The comparison of solutions must have been made by either Nessler tube or Duboscq colorimeter. Bird and Newsome employed colorimetric analysis of solutions of the purple tin lake.

dyed under similar conditions with the test sample. The "reduced" mordant is assumed to adsorb only hæmatein, while the "oxidised" mordant adsorbs hæmatoxylin as well. Thus, by comparison with a suitably graded series of control dyeings from pure hæmatein, the composition of the sample in terms of pure colouring matter may be determined. It is evident from Table I that this method is reliable, even though the soundness of its theoretical basis seems doubtful.

(iv) TENSIOMETRIC ANALYSIS—Preston's method [20] was tried, with cetylpyridinium bromide as titrant. The end-point was sharp, but gave values much higher than theoretical (assuming that a 1 : 1 complex is formed).

Three methods of analysis were used for the colouring matter in residual bath liquors—

(i) Direct colorimetric analysis after making the liquors slightly alkaline with ammonia

(ii) Electrometric (back) titration with titanous chloride

(iii) Colorimetric determination of a solution of the coloured fibre. Nylon was dissolved in *m*-cresol, and wool (1 g.) was dissolved in 10% (wt./vol.) potassium hydroxide (25 c.c.), followed by dilution with distilled water, using as calibration standards known solutions of colouring matter and wool similarly prepared.

In some cases the results of method (iii) were checked by analysis of the residual liquors by method (ii), the agreement being good.

Hæmatoxylin

Several methods of absolute analysis were examined, e.g.—

(i) IODINE METHOD—The reaction is as follows—

$$C_{16}H_{14}O_6 + I_2 = C_{16}H_{12}O_6 + 2HI$$

To 50 c.c. of a 0·1% aqueous hæmatoxylin solution, 2 c.c. of 4 N. acetic acid, 20 c.c. of 2 N. sodium acetate, and excess of 0·1 N. iodine solution were added, and the mixture was titrated against standard sodium thiosulphate, using starch indicator.

(ii) PEROXIDE METHOD—The sample was added to a solution of hydrogen peroxide, potassium iodide, and sulphuric acid, and the mixture titrated against standard sodium thiosulphate solution, after shaking for a few minutes.

(iii) DICHROMATE METHOD—The sample (50 c.c. of 0·1% aqueous solution) was titrated with 0·1 N. potassium dichromate solution in presence of 10 c.c. of 10% Rochelle salt solution and 20 c.c. of 4 N. sulphuric acid, in an inert atmosphere. The solution changes from yellow through dark green to violet, and the end-point is best determined potentiometrically. This method gave slightly higher values than (i) and (ii), e.g. 96·6% for a sample containing 2·5% water removable by normal drying.

The other methods tried were potentiometric titrations with potassium dichromate (in presence of Rochelle salt and sulphuric acid), and with iodine (as above), potassium ferricyanide, or ammonium ceric nitrate respectively. The last three did not give very satisfactory results.

For the comparative analysis of adsorption liquors two methods were used—

(i) COLORIMETRIC—The deep blue water-soluble lake was formed by addition of approximately the theoretical amount of potassium chromate (see Part II) and warming for 60 sec. at 60°C., followed by dilution with water and measurement on the absorptiometer with an Ilford Spectrum filter No. 607 (orange). In the experiment in which solutions with a range of pH values were used, it was necessary to adjust the solutions to pH 5·9 by cautious addition of ammonia before adding the potassium chromate. The method gave consistently reliable results with the pure solutions used for calibration, but sometimes returned erratic results when used with the solutions from the adsorption tests. The reason for this behaviour was not ascertained, but it may have been that traces of fibre decomposition products interfere with lake formation.

(ii) REFRACTOMETRIC—The refractive index of the solutions was measured, without dilution, on a refractometer; calibration of the instrument readings with hæmatoxylin solutions of known strength gave a linear relation between square of refractive index and concentration. The results are readily reproducible and do not seem to be affected by the traces of hæmatein which are formed during the experiments (colouring the solution pale brown); for identical adsorption data were obtained whether the reducing agent was present or not, except with nylon (Fig. 2), and in this case it is presumed that the reducing agent (hydroxylamine sulphate) acts as a swelling agent for the fibre.

Tetramethylhæmatoxylin

This was determined in the adsorption tests by refractometry.

Electrometric Titration of Hæmatein

Hæmatein (0·1 g.) was pasted with 25 c.c. Cellosolve, and the solution diluted to 250 c.c. with boiled distilled water. The liquid was titrated electrometrically at room temperature, with 0·0114 N. potassium hydroxide solution in a stream of nitrogen, using the glass and calomel electrodes (Fig. 4).

ADSORPTION EXPERIMENTS

For most of these, except those made at the boiling point, the fibre samples (1 g.) were each treated with 20 c.c. of liquid in test tubes, tightly stoppered or completely sealed in the flame, fixed by phosphor-bronze spring clips to a shaft mechanically rotated at 35 r.p.m. under water in a thermostat tank, so that they were given a constant and regular end-over-end agitation. Even so, when loose fibres are used, some difficulty is experienced in obtaining adequate penetration of the liquid and movement of the fibres, which tend to stick as a lump at the end of the tube. This difficulty was surmounted by use of a perforated glass tube fibre-

holder, of caterpillar shape (Fig. 7), designed to fit loosely inside the test tube. The fibre is packed into the holder, and the ends, if the tube is large, are plugged with glass wool or polythene (in small tubes no plug is necessary, and the ends need not be tapered). During agitation the holder falls to and fro in the test tube, with a regular motion out of phase with the movement of the liquor, which is thus caused to pulsate into and out of the fibre via the perforations.

FIG. 7—Perforated Glass Tube Fibre Containers for Adsorption Experiments in the Liquid Phase (scale approx. 1 : 1)

Hæmatoxylin

Hæmatoxylin oxidises to hæmatein so readily that its aqueous solutions in absence of a reducing agent are always pale yellow or brown. The anion is the active species, and consequently proton-acceptors will promote oxidation. Thus it was observed that in prolonged contact with nylon or wool, but not with cellulose or cellulose triacetate, in the adsorption tests, the solutions darkened considerably (the fibres also becoming coloured brown). Colorimetric checks against solutions of hæmatein of known strength showed that the actual proportion of hæmatoxylin oxidised was quite small, being of the order of 5%. Nevertheless, a number of tests were made to examine the use of reducing agents for preventing oxidation during the tests. Sodium hydrosulphite and hydroxylamine sulphate were found to be effective, but both compounds appeared to interfere with lake formation in the colorimetric analysis. Using refractometric analysis, however, in comparative trials with wool, it was found that the amount of hæmatoxylin adsorbed was not materially affected whether the reducing agent was present or not (Fig. 1). Evidently any hæmatein formed does not interfere with the adsorption of hæmatoxylin. The reducing agent when used with nylon considerably increased the adsorption (Fig. 2), presumably by acting as a swelling agent for the fibre.

Even with the most careful precautions, however, the individual adsorption tests with hæmatoxylin, particularly on nylon and wool, seem to be liable to appreciable random errors (see Fig. 1 and 2), but the general form and the position of the isotherms are reasonably reproducible.

Hæmatein and Brazilein

The pure colouring matter (2·0 g.) was pasted with Cellosolve and added to boiling distilled water (1 litre), after addition of a trace of sodium hydrosulphite to remove oxygen. After boiling for 15 min. to effect complete solution, the liquid was allowed to stand a few hours, filtered, and stored under carbon dioxide in a well stoppered bottle. For preparing the baths at low pH values both the stock solution of colouring matter and the water used for dilution were first brought to the same pH value with dilute sulphuric acid. To remove air and minimise oxidation a brisk stream of carbon dioxide was passed through the liquor for 2 min. just before closure of the tubes by rubber stoppers. For experiments at the boiling point, flasks and reflux condensers were used, and a gentle stream of carbon dioxide was passed into the liquor throughout the experiment and allowed to escape up the condenser.

AIR OXIDATION OF HÆMATEIN— FASTNESS PROPERTIES OF HÆMATEIN DERIVATIVES

Anomalous results were obtained from some preliminary adsorption experiments with hæmatein; the anomalies were found to be caused by air oxidation of the colouring matter. Further investigations were made into this phenomenon, in which solutions of pure hæmatein, brazilein, and monobromo- and monochloro-hæmatein were prepared at normal dyebath strengths in buffers of various pH values and were heated under reflux without exclusion of air, at 90–95°C. for periods up to 48 hr. Samples were examined at intervals on the absorptiometer and, in some cases, complete absorption curves were plotted by the ultraviolet spectrograph. The colour of the hæmatein and brazilein solutions at pH values between 2 and 5 steadily deepened over the whole period, but at pH values above 5 there was first a deepening of colour, and then after 15 hr. the colour became lighter. When the experiments were repeated in boiled water under carbon dioxide little or no change in colour occurred. Consequently, the quantitative experiments subsequently carried out to test the adsorption behaviour of hæmatein and brazilein on fibres were, as just described, made in an inert atmosphere. The bromo and chloro derivatives were stable even in presence of air.

It was apparent that, even during the normal period of dyeing, some decomposition of hæmatein must occur in the commercial dyebath, which might adversely affect the hue or fastness properties of the dyeing. A study of the colours and light fastness values given by making variations in the mordanting and dyeing procedure for hæmatein itself, and by using certain of its derivatives in place of hæmatein, was therefore carried out to determine whether the normal light fastness value could be improved. The results may be summarised as follows—

No appreciable improvement in colour or light fastness of patterns mordanted with "reduced chrome" was obtained by—

(*a*) substituting pure hæmatein for commercial logwood extract in equivalent amounts

(*b*) dyeing under carbon dioxide to prevent air oxidation

(*c*) using the monobromo or monochloro derivatives of hæmatein, hæmatein monomethyl ether, or *iso*hæmatein chloride in place of hæmatein. The bromo and chloro

compounds give redder, and *iso*hæmatein chloride much redder, blacks than hæmatein itself.

LOAD–EXTENSION DIAGRAMS

These were made on a Cambridge Instrument Co. extensometer maintained in a controlled atmosphere at 20°C. and 65% R.H. Single fibres (2 in.) from the Lincoln fleece used throughout this work were tested. Untreated fibres were soaked in distilled water before use, and a drop of water was run on to them when they were clamped in the apparatus. Treated fibres were taken straight from bulk samples which had been agitated for 24 hr. at 60°C. with solutions of the two solutes. They contained 280 mmol. of hæmatoxylin and 850 mmol. of phenol respectively per kilogram, and before extension were wetted by pipette with the solutions from which they had just been removed.

OTHER APPARATUS USED

pH measurements were made on a Marconi glass electrode; refractive index measurements with a Zeiss Pulfrich refractometer; and absorptiometric measurements on a Hilger Spekker photoelectric absorptiometer. Ultraviolet spectra were photographically recorded on a Hilger quartz spectrograph and measured on a Hilger Spekker photometer.

APPARENT HEAT OF ADSORPTION

This was calculated in the usual manner from the isotherms by the Clausius–Clapeyron equation—

$$\Delta H_{\text{a}} = \frac{RT_1T_2}{T_1-T_2} \ln \frac{C_1}{C_2}$$

where C_1, C_2 are the respective concentrations of the baths at equilibrium at two temperatures T_1, T_2 with the same concentration in the fibre.

PADDING PROCESS

The good solubility of hæmatoxylin and the results of the adsorption and lake-forming experiments suggested that the compound could be applied satisfactorily to wool from a fairly strong aqueous solution by padding, the lake thereafter being formed by passing the treated fabric immediately into a boiling solution of potassium chromate. This proved to be practicable on the laboratory scale, but no further trials of the method were attempted.

* * *

We extend our thanks to Dr. (late Professor) W. M. Cumming, at whose suggestion we first undertook the investigations described in this and the succeeding paper; and to Professor P. D. Ritchie, for his interest and encouragement throughout the later stages of the work. Other acknowledgments are made in Part II.

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A Study of Certain Natural Dyes

II—The Structure of the Metallic Lakes of the Brazilwood and Logwood Colouring Matters

F. M. ARSHID, R. F. CONNELLY, J. N. DESAI,
R. G. FULTON, C. H. GILES, AND J. C. KEFALAS

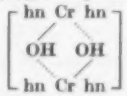
The lake-forming reactions of the oxidised and reduced forms of the logwood and brazilwood colouring matters with the more important mordanting metals have been investigated. The oxidised forms appear to be the lake-forming species, the *o*-hydroxyquinone system of the molecule chelating with the mordanting metal atom; the leuco forms must first be oxidised by air or the mordanting salt before lake formation can take place. When a chromate or a dichromate is used as mordant, this is first reduced to the chromic cation, at the expense of the total destruction of some of the colouring matter, before lake formation occurs.

The logwood colouring matter, when treated with a chromium salt in solution or on the fibre, forms a deep blue 2 : 1 (dye : metal) complex, which is preceded by a transient purple 1 : 1 complex. Aluminium, cobalt, and (ferric) iron also form 2 : 1 complexes, and copper appears to form a 1 : 1 complex.

The lakes formed in substance are amorphous, infusible, and almost insoluble in all solvents. Exact characterisation of these bodies, which appear to be mixtures, is not practicable, but by a consideration of probable reaction sequences, in conjunction with the elementary analyses, a series of formulæ have been drawn up which are believed to represent their most probable constitutions. The development of insolubility is believed to be due to one or more of the following effects—mutual precipitation of cationic or anionic lakes by complex anions or cations respectively, formation of non-ionic lakes, and the form of condensation polymerisation known as "olation".

It is suggested that similar changes occur in the fibre during the normal mordanting and dyeing processes, and that parallel reaction sequences may take place in dyeing other forms of mordant dye.

The deep blue–black logwood lake on the fibre is believed to be a mixture of an anionic complex, e.g. $[hnCr(OH)_2hn]^-\ [Cr(OH)_2(H_2O)_4]^+,\ 4H_2O$ with the derived olated body—



$8H_2O$ (hn = Hæmatein anion)

The iron lake is probably similar in constitution.

In addition to the action of the chelating groups, the phenolic groups not in the quinonoid nucleus of the colouring matter molecule appear to take part also in salt formation with cobalt or copper, but not with chromium or iron.

The logwood and brazilwood colouring matters are of no value unless combined with a metallic mordant: only then do they develop full colour and fastness properties. The reactions they undergo in the mordanting processes either in presence or in absence of the fibre have not previously been fully elucidated, and as they are of both theoretical and technical interest and importance, an investigation into their mechanism was undertaken. Indeed, not a great deal is known of the reactions which take place when any other type of mordant dye is treated with metallic mordanting compounds on the fibre, and it was hoped that some of the conclusions reached in the present research might throw light upon this wider aspect of the subject.

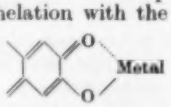
We owe principally to Morgan and Drew and their collaborators [4,11], and to Boyle, Cumming, and Steven [4b], our knowledge* of the constitutions of many metallic lakes of synthetic dyes, but the present compounds differ considerably in structure from the synthetic materials, and so they may be expected to differ from them to some extent also in lake-forming characteristics.

Theoretical

THE NATURE OF THE REACTIVE GROUPS CONCERNED IN LAKE FORMATION

The oxidised forms, brazilein and hæmatein†, rather than the leuco compounds, appear to be the lake-forming agents. Lakes can be formed from the leuco compounds, but the reactions almost certainly involve their prior oxidation by air and/or the metal salt used. In illustration, the relative lake-forming tendencies of hæmatoxylin and hæmatein can be demonstrated in a rather striking way by boiling, in an open beaker, an aqueous solution of the former containing some aluminium chloride and a little sodium hydrosulphite to ensure absence of oxygen. After a time the clear colourless solution becomes turbid, owing to the formation of a white precipitate of sulphur and instantly afterwards it becomes deep purple. Purple is the colour of the aluminium lake, which clearly cannot be formed until all the reducing agent has been destroyed by air and the hæmatoxylin has thus been left free to be oxidised by air to hæmatein.

Further, the anions of the colouring matters, rather than the neutral molecules, must be the reactive species, because lake formation is promoted by alkaline conditions and retarded in acid solutions. The retardation in acid must be due to competition for the dye anion between the metal cation and the hydrogen ion of the acid. The dye anions are formed by ionisation of the *o*-hydroxyquinone system in the oxidised forms, and this system will therefore be responsible for lake formation by chelation with the metal atom—



* For a short summary see Giles [7].

† For formulæ see Part I.

The additional phenolic groups in the molecule must also be considered*; of these, brazilein has one and hæmatein two. In certain circumstances these also might react with a metal atom or atoms, especially those in hæmatein, which, being *ortho* to each other, might form an additional chelating centre. Morgan and Smith[11] found that, when two potential chelating centres are present in an anthraquinone dye molecule, only one forms a true chelate ring on treatment with a cobaltammine salt, the other, only partly reactive, forming a salt linkage. Weinland and Dottinger[16], and Weinland and Walter[17], by treating alkaline catechol solutions with metal salts, obtained chelate compounds of the type $[M(C_6H_4O_2)_2]^{-}2K^{+}$ where M = Co^{2+} or Cu^{2+}, and of the type $[M(C_6H_4O_2)_3]^{3-}3K^{+}$ (M = Cr^{3+}); and Shuttleworth[14] examined the reactivity of phenol itself and of several di- and tri-hydric phenols with a basic chromic sulphate: only those having two phenolic groups in the *ortho* position formed complexes with the salt. Our own results, discussed below, are consistent with some combination of phenolic groups in hæmatein and brazilein with copper or the cobaltammine cation, but no definite evidence has been found that they react with chromium or iron.

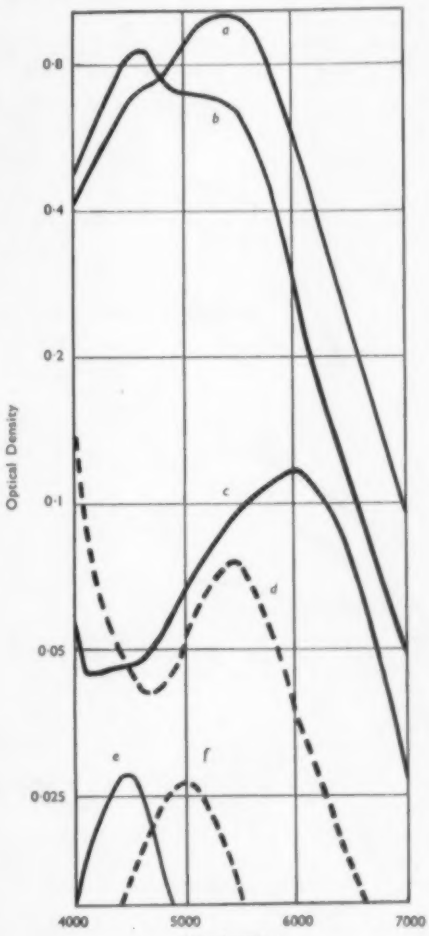
COLOUR REACTIONS OF HÆMATEIN SOLUTIONS WITH CHROMIUM AND ALUMINIUM SALTS

Both the aqueous and the alcoholic solutions of brazilein and hæmatein are brownish in colour, becoming deep cherry-red on addition of alkali. When the alcoholic solutions are boiled with a chromic salt, e.g. chromic chloride, they slowly change to a purple colour, identified below as due to the presence of a (cationic) 1 : 1 dye–metal complex. Aqueous solutions show a similar change, but this takes place much more slowly, presumably because of the greater degree of ionisation and hence of acidity therein.

This 1 : 1 complex can thereafter react with another dye anion to form the (anionic) 2 : 1 complex, which is blue. (The constitution of this complex is discussed below.) This change does not seem to occur readily in alcoholic or ethoxyethanolic (Cellosolve) solutions, but it does so very readily in neutral or alkaline aqueous solution. The reactions are in fact so rapid under those conditions that the purple 1 : 1 complex is formed instantaneously when potassium chromate solution is added to hæmatein solution in the cold, and on warming the colour changes at once to that of the blue 2 : 1 complex.

All these colour changes are illustrated by the light absorption curves shown in Fig. 1. Hæmatein in ethanol or water (curve *e*) has an absorption peak at 4550 A. which shifts to 5000 A. in ammoniacal solution (curve *f*). The purple lake has a peak at 5400 A. in ethanol (curves *a*, *b*) or water (curve *d*), and the blue lake has one at 6000 A. (curve *c*). All the lake solutions show evidence of the presence of unchanged hæmatein (slight maxima at 4550 A.); those formed with chromate show the commencement of the ultraviolet absorption curve of the unchanged chromate ion, and the same type of solution after warming shows possible evidence of the presence of the 1 : 1 as well as the 2 : 1 lake.

Aluminium chloride forms a water-soluble purple lake with hæmatein.



(*a*) Hæmatein (1 mol.) + *Cr* (3·25 atoms, as $CrCl_3,6H_2O$)
(*b*) As (*a*), but with 0·55 atom of *Cr*.
(*c*) Binary aq. soln. of hæmatoxylin + K_2CrO_4, after heating
(*d*) The same as (*c*), when first mixed, cold
(*e*) Hæmatein alone, in water
(*f*) Hæmatein alone in dil. aq. ammonia
(Concentrations of solutions have arbitrary values, chosen so that the curves may be separated, for clarity. The ordinates being logarithmic, the shape of each curve is the same at any concentration.)

FIG. 1—Light Absorption Curves of Solutions of Hæmatein and its Chromium Lakes

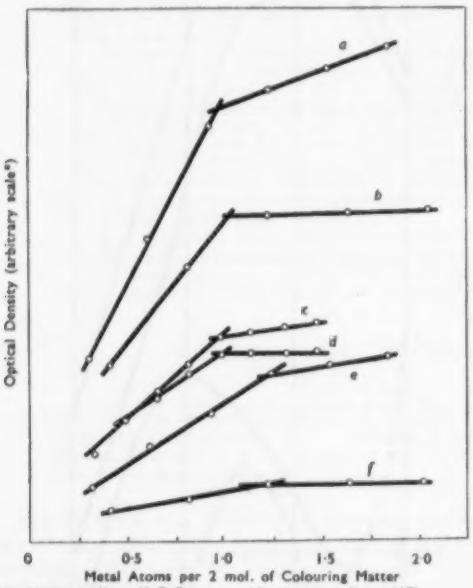
CONSTITUTION OF THE BLUE HÆMATEIN–CHROMIUM AND PURPLE HÆMATEIN–ALUMINIUM LAKES

The colouring matter : metal ratio of these lakes formed in solution was determined by a colorimetric method as follows. A series of solutions of hæmatein or hæmatoxylin were prepared, each containing the same amount of colouring matter but increasing quantities of metal salt,

* The alcoholic group will probably not react with metals: the colour of the chromium lake is not significantly affected when this group is alkylated[5].

After being boiled to complete the lake formation, the solutions were diluted and their optical densities at the peak absorption wavelength of the lake determined on the absorptiometer. Curves were obtained consisting of two straight lines intersecting at the point corresponding to the complex ratio (Fig. 2). The optical density rises as more lake is formed, until all the colouring matter has reacted*.

If the ratios so calculated (Table I and Fig. 2) are examined, it is seen that they tend towards 2 : 1

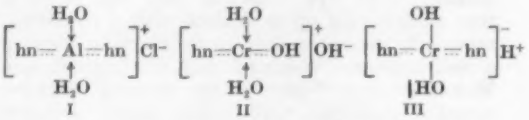


(a) Hæmatoxylin + K_2CrO_4 (d) Hæmatoxylin + $AlCl_3$
(b) Hæmatein + $K_2Cr_2O_7$ (e) Hæmatein + K_2CrO_4
(c) Hæmatein + $AlCl_3$ (f) Hæmatoxylin + $K_2Cr_2O_7$

FIG. 2— Colorimetric Determinations of Metal : Dye Ratio in Water-soluble Logwood Lakes

*Several of the curves have been displaced vertically, for clarity

(dye : metal) in every case. Disturbing factors must, however, be affecting the formation of these complexes, because none of the ratios is a simple integer. This can be accounted for as follows: The chromate or dichromate ion must first be reduced to the chromic salt state, and this means that some colouring matter must be oxidised and destroyed† before the remainder can enter into complex formation. The effect will be to *increase* the apparent dye : metal ratio. This is, in fact, seen in three of the lakes listed in Table I. The small increase that is actually observed indicates a very complete destruction of a proportion of the hæmatoxylin or hæmatein concerned. Two of the other three lakes, however, give ratios appreciably less than the theoretical. These three, all chromium lakes, are observed to be formed less readily in the boiling solutions than that from hæmatoxylin and chromate, and the low ratios can be accounted for by the presence of a proportion of the purple (1 : 1) lake, which, as already mentioned, is perhaps detectable by spectrographic analysis (Fig. 1). The blue chromium lake is anionic (see Experimental Section) and the aluminium lake is cationic. We may, therefore, formulate these complexes, as they exist in the dilute solutions, as follows (I–III)—



I II III

TABLE I

Analytical Ratios of Water-soluble Logwood Lakes

Colouring Matter (D)	Metal Salt (MX)	Complex Ratio M : 2D*	Complex Ratio D : M
Hæmatoxylin	$AlCl_3$	0·98	2·05
	K_2CrO_4	0·98	2·05
	$K_2Cr_2O_7$	1·25	1·60
Hæmatein	$AlCl_3$	0·98	2·05
	K_2CrO_4	1·25	1·60
	$K_2Cr_2O_7$	1·03	1·95

* See Fig. 2.

CONSTITUTION OF THE PURPLE HÆMATEIN–CHROMIUM LAKE

This is considered to be a 1 : 1 complex for the following reasons— (*a*) the elementary analyses of the material prepared in substance (see Experimental Section) are consistent with complexes of this nature; (*b*) it is an intermediate stage in the formation of the 2 : 1 dye–metal lake, which is most likely to take place by the route of successive bimolecular reactions of addition of dye anion to the metal atom; (*c*) its colour is consistent with a less complex structure than that of the blue 2 : 1 lake.

The colorimetric method of analysis used for the blue lake could not be employed with reliance for the purple chromium lake, because the low reaction rate in alcoholic solutions makes the point of attainment of equilibrium uncertain; and in aqueous solutions, with potassium chromate as chelating agent, the purple compound is unstable and very rapidly changes to the blue.

LAKES PREPARED IN SUBSTANCE

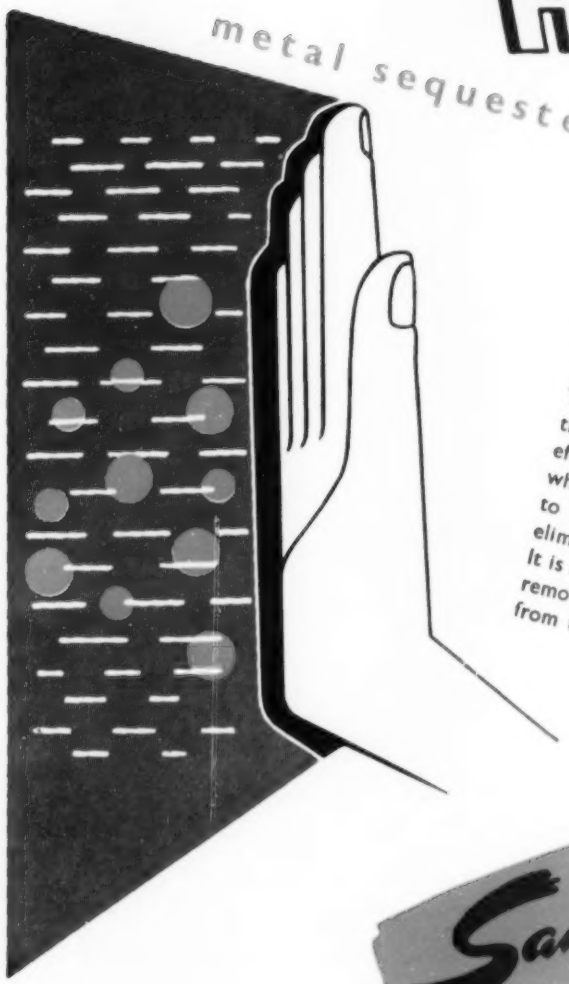
Analysis of the lakes in solution gives reasonably conclusive evidence regarding their constitutions. This is not so with those prepared in substance, for once dried, they become virtually insoluble in all solvents, except by destruction in concentrated mineral acids and alkalis. We attribute their insolubilisation to the operation of one or more of three processes— (*a*) formation of simple neutral, unionised complexes. Such complexes are an intermediate stage between the cationic and anionic forms and are likely to be less soluble than either of these— the analytical data support the assumption that they occur in some of the materials prepared, (*b*) formation of complex salts between cationic lakes and anions of colouring matter, and (*c*) olation (see below).

* The further slight rise in some of the solutions is evidence of the formation of an increasing proportion of 1 : 1 complex with increase in added chelating salt.

† This applies to both hæmatein and hæmatoxylin. Even the oxidation of two moles of the latter to hæmatein is insufficient to reduce one mole of chromate or half a mole of dichromate to the chromic (Cr^{3+}) state.

PLEXINE HBW

metal sequestering agent



Plexine HBW is a sequestering agent which forms with metal ions complex compounds which are stable to prolonged boiling. The metal ions are thereby rendered ineffective and troubles which can occur due to their presence are eliminated.

It is also useful for the removal of metal stains from textile materials.

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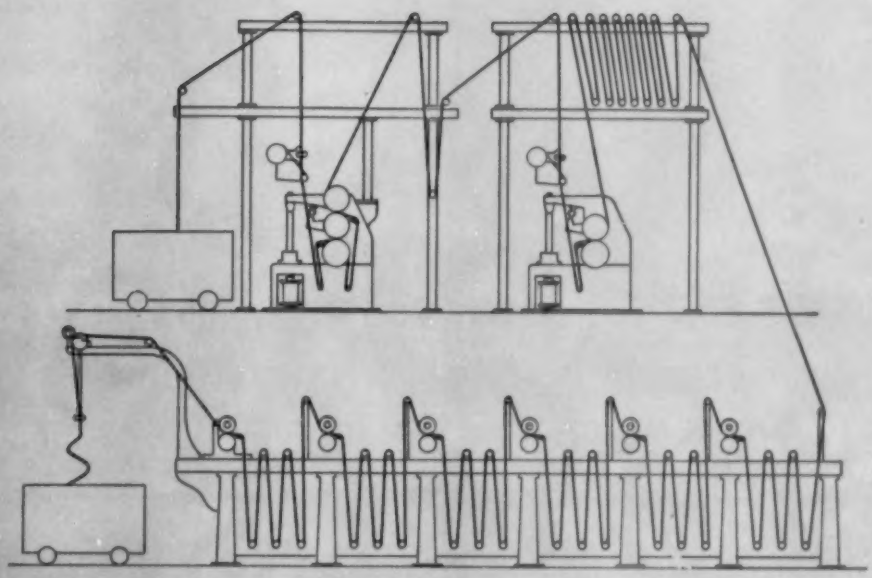

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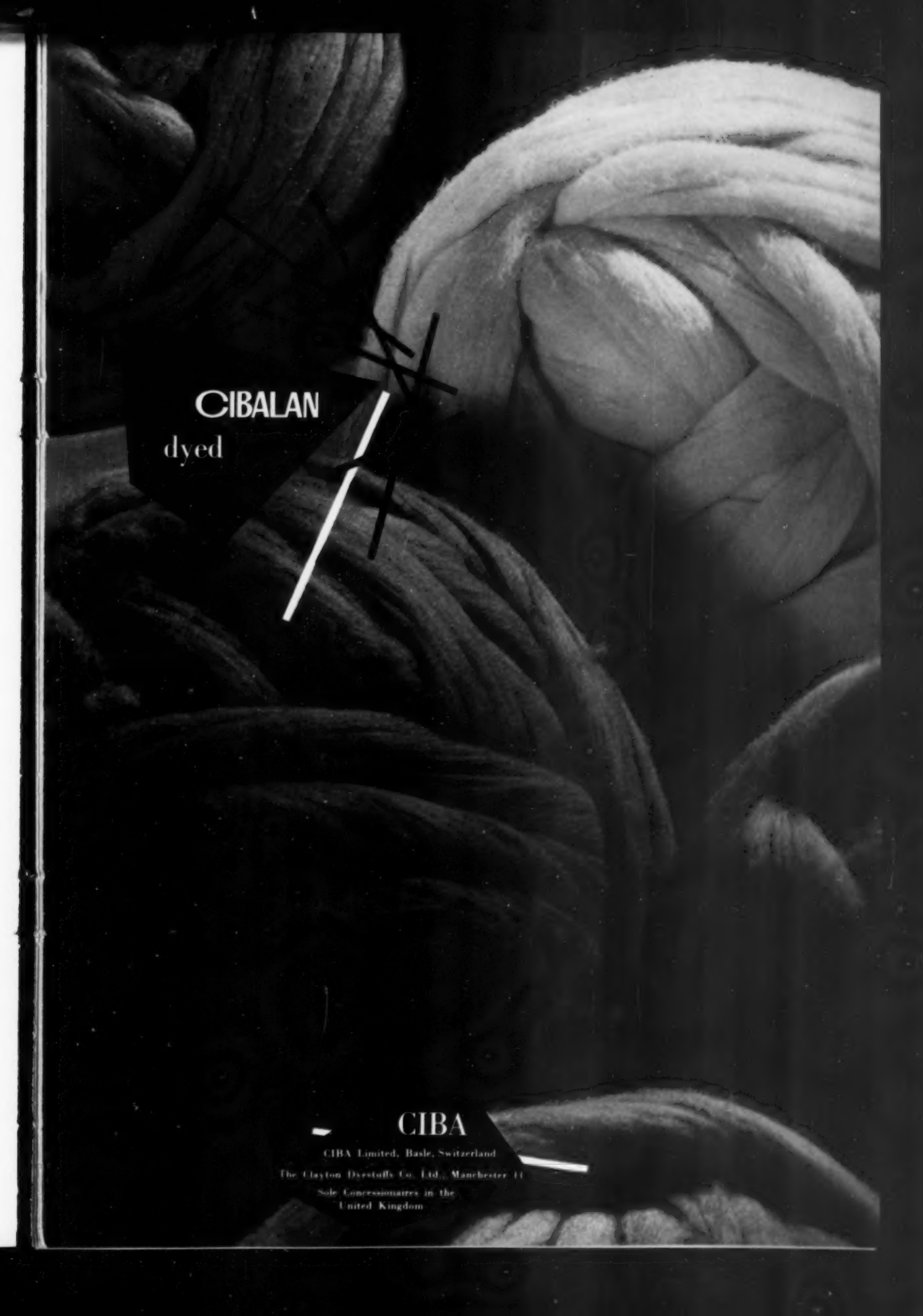
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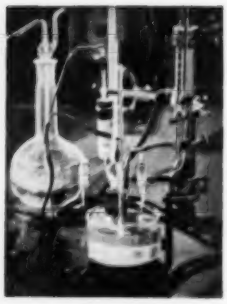

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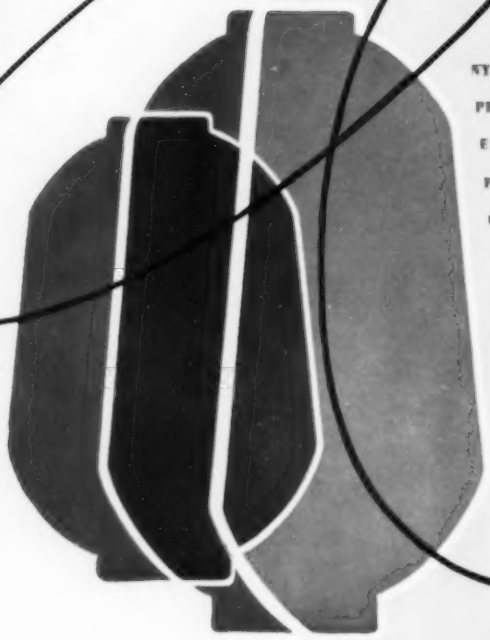

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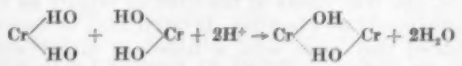
The only means of determining the composition of these products is by a study of their elementary analyses together with the probable reaction sequence in their formation. None of the analyses, in fact, is exactly consistent with any probable single formula, and it must be assumed that the products are mixtures. In many cases a reasonably consistent analysis is returned by successive preparations, in others it is not so. Nevertheless, an attempt has been made to establish the most probable constitution of each product prepared, by computing the theoretical analyses of mixtures of compounds of all the most likely constitutions, until a value is found which fits the experimental figures. Analytical details are given below, and a list of the probable formulæ involved (IV–XII) is included as an Appendix.

Lakes from Chromic Salts

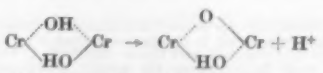
The substances obtained from hæmatein and brazilein by reaction with normal (hexa-aquo-) chromic chloride $[Cr(H_2O)_6]Cl_3$ or chromic fluoride have analyses and properties consistent with compositions of cationic lakes corresponding to 30 parts of IV*a* and 70 parts of IV*b*, and 67 parts of V*a* and 33 parts of V*b*, respectively. When a salt is employed in which some chlorine is in the inner complex, e.g. $[CrCl_2(H_2O)_4]Cl$, such chlorine is retained by the metal and is found in the lake. The analyses in this case suggest the presence of some cationic and some neutral non-ionic lake, and the properties and analyses of the products are consistent with mixtures of 70 parts of VI*a* with 30 parts of VI*b* for the hæmatein derivative, and 25 parts of VII*a* with 75 parts of VII*b* for the brazilein derivative, though it may well be that more complex mixtures than these are, in fact, present. The actual compositions obtained must be dependent, amongst other conditions, upon the physical state of the reactants, which, at least in the case of brazilein, are not wholly in solution at the start of the reaction.

Lakes from Chromate, Dichromate, etc.

When dilute solutions of the water-soluble blue chromic lake are evaporated to dryness, the lake cannot be redissolved in water; some solutions of the lake have been observed to flocculate out of solution in the cold on standing for several days. These facts point to the operation of the form of condensation polymerisation known as *olation* (Stiasny, 1931)[10], which takes place slowly in aqueous solutions of inorganic chromic salts, e.g. chromic sulphate, on standing or on heating, e.g.—



On prolonged treatment, olation in such solutions may be followed by the so-called "oxolation" process—



We are not aware that these processes have previously been considered to take place in solutions of organic chromium lakes, but there appears no reason to doubt that they could do so. A consideration of the above equations will show that, if they do in fact occur in the blue anionic lake solution, this should become at first increasingly alkaline and then increasingly acid; moreover, these changes might take place very slowly, as they are known to do in the inorganic salt solutions. Examination of the changes in pH of such lake solutions with time (Fig. 3) does in fact give evidence of this behaviour. The pH value at first rises by about 0·5 over a period of some 25 hr. at 47°C.* and then steadily falls. (The changes are not in any way connected with air oxidation effects, because they were found to take place in the same manner when air-free solutions were refluxed under nitrogen).

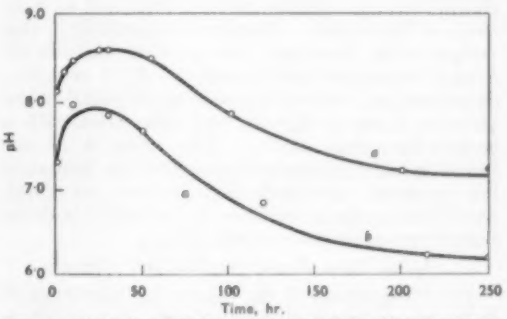


FIG. 3— Change in pH Value of Solutions of the Blue Chromium-Hæmatein Lake. Temperature 47°C. 100 c.c. of 0·1% aqueous hæmatoxylin solution, (*a*) + 25 c.c., and (*b*) + 32 c.c., of 0·1% aqueous K_2CrO_4 solution

If the same reactions occur when the lake solutions are concentrated and evaporated to dryness, the insolubility of the final products of reaction of the colouring matters with chromium, and perhaps also iron salts, could be accounted for. The analyses of the chromium (and iron) lakes of hæmatein or brazilein are in fact consistent with mixtures of olated complexes (e.g. VIII*b*, IX*c*), in admixture with roughly equal proportions of corresponding anionic (unolated) complexes, complex chromium cations being associated with the latter (VIII*a*, IX*b*). On account of the much-slower formation of the oxolated body, it seems unlikely that much of it is present under normal conditions.

The lake prepared from hexa-amminochromic nitrate and hæmatein in water appears to have the same composition as that made from a dichromate. All the ammonia molecules associated with the chromium atom are thus displaced by either hæmatein or hydroxyl ions †.

Lakes from Hexa-amminocobaltic Chloride

This salt was used extensively by Morgan and Smith[11] in their investigations of the structure of lakes of dyes. Its especial value lies in its twofold action: with it chelating groups form normal chelate complexes, but monobasic salt-forming

* About 2 hr. at b.p. (results not shown here).

† This is consistent with the fact that neutral nitrogen and negative oxygen have about equal co-ordinating affinity for metals[9], and both probably have more affinity than neutral water molecules, so that, for example, a co-ordinated ammonia molecule would not be displaced by a water molecule, but might be displaced by a hydroxyl ion or a hæmatein anion.

groups, and even in some cases phenolic groups, displace one ammonia molecule from the cobalt atom, so that an analysis of the product for cobalt and nitrogen or ammonia can show which acidic groups of the dye molecule are chelate-forming and which are salt-forming. The hæmatein and brazilein lakes contain nitrogen, and some substitution of free phenolic groups has thus taken place. The analyses suggest that the products are mixtures of 2 : 1 complexes, and the data are consistent with the hæmatein product being a mixture of 10 parts of X*a* with 90 parts of X*b*, and the brazilein product 20 parts of XI*a* with 80 parts of XI*b*.

Lakes from Cupric Sulphate

These are readily formed as dark blue or violet precipitates by addition of the metal salt to solutions of hæmatein or brazilein respectively. One sample of the hæmatein lake gave an analysis for copper corresponding to a cationic 1 : 1 complex, containing an additional copper atom bound to the phenolic hydroxy groups, and associated with a hæmatein anion (XII). The samples of the brazilein lake and another sample of the hæmatein lake returned excessively high analyses for metal, attributed to the presence of hydroxide or perhaps some cuprous or basic cupric salts.

Lakes from Ferric Ammonium Alum

The composition of the hæmatein lake appears to be very similar to that of the products from potassium dichromate: i.e. it is probably a mixture of olated and anionic 2 : 1 complexes (VIII*a*, VIII*b*: M = Fe). The brazilein lake also resembles that made from potassium dichromate.

ATTEMPTED PREPARATION OF MODEL COMPOUNDS

It was hoped that the use of simpler bis-*o*-dihydroxy phenolic compounds would enable the proposed structures of the metallic lakes of hæmatein and brazilein to be confirmed. A number of preparations of such compounds were attempted, but were abandoned owing to the practical difficulties involved.

GENERAL SEQUENCE OF REACTIONS IN LAKE FORMATION

A study of the suggested nature and proportions of the components of the various lakes (IV–XII) reveals a certain regularity of pattern in the sequence of chemical changes leading to their formation. Three main trends may, in fact, be observed in these changes— (*a*) Co-ordinated ammonia or water molecules, or chlorine atoms, attached to the metal atom may be replaced by colouring-matter anions and/or by hydroxyl ions*, with a consequent decrease in the positive charge on this atom. Eventually this charge becomes negative. (*b*) Olation commences when two hydroxyl ions have been added to the metal atom, and the complex has become negatively charged. The olation process does not appear to go to completion: the products contain considerable amounts of unolated material. (*c*) The final product is usually a mixture containing a preponderating amount of the least soluble of the components present.

* This is known to take place in either aqueous or alcoholic solution.

NATURE OF THE LAKES IN THE FIBRE

The various mordanting metals all give shades of dull blue or reddish blue with logwood colouring matters on the fibre, deepening to black with a characteristic bluish or purplish cast in the heaviest dyeings. The brazilwood colouring matters when mordanted are dull purple or purple–brown in tone.

The processes which produce the inert, insoluble lakes when the aqueous reaction mixtures are evaporated to dryness must also operate when mordanted and dyed fibres are dried. We thus expect that the lakes in fibres will be very similar complex mixtures to those whose composition we have already discussed*, and the full formulation of the most important product, logwood black on a dichromate mordant, in the olated form is probably close to that shown in formula XIII.

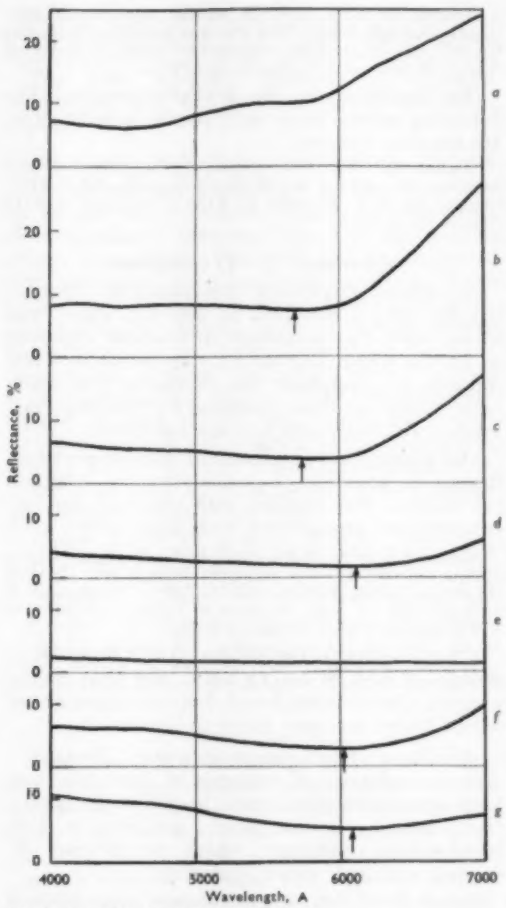
During the dyeing process the simpler anionic 2 : 1 lake may be formed in the fibre†, and indeed aqueous solutions of this lake will dye wool the characteristic navy blue which logwood displays at low depths. Before the blue complex is formed, however, it is preceded by the formation of the purple 1 : 1 complex, and if patterns dyed with logwood on a chrome mordant are examined during the first few minutes of immersion in the bath the colour is seen to be dull purple, which later changes to blue or blue–black. In order to study these changes more precisely, a number of wool patterns mordanted and dyed with hæmatein under different conditions were examined spectrophotometrically. The reflectance curves are low and rather indeterminate (Fig. 4), but the following conclusions can be drawn from them—

The purple colour in the early stages of dyeing represents a mixture of cationic 1 : 1 lake and free hæmatein anion (Fig. 4 *a–d*), but these soon combine together to form the blue 2 : 1 complex (Fig. 4 *d*, *e*). This can be confirmed by removing a purple pattern from the bath and boiling it in water. Its colour then changes to blue (Fig. 4*f*), but if the fibre remains in the dyebath this change is complete in 5–10 min. A similar sequence of events takes place when chrome alum is used as mordant, but the blue lake then forms more slowly and the dyed patterns, even after normal dyeing periods, have a pronounced reddish tone.

Clearly the metal salt and the colouring matter are at first absorbed by the fibre more rapidly than they can combine to form the lake, but as their concentration in the water inside the fibre increases, so does their rate of interaction, so that after 5–10 min. the lake forms in the fibre as rapidly as the components are absorbed. It can readily be demonstrated that when wool is boiled in mixed weak aqueous solutions of colouring matter and mordant, lake formation is much more rapid in the fibre itself than it is in the solution in absence of fibre.

* Race, Rowe, and Speakman[12] found that the ratios of dye molecules to chromium atoms in chrome-mordanted wool dyed with several typical synthetic dyes were almost exactly 2 : 1. Their measurements were made by comparing the amount of dye absorbed with the amount of non-extractable chromium. This method would give exact 2 : 1 ratios even if the actual lakes were polymerised structures of the type proposed here.

† Dichromate is reduced to the chromic state by wool itself[2], and thus less actual destruction of colouring matter by this reagent may occur on the fibre than in solution.



(*a*) Dyeing of 3% Hæmatein, unmordanted
(*b*) Fabric mordanted in acid potassium dichromate, then dyed for 30 sec. with hæmatein (3% on wt. of fabric)
(*c*) As (*b*), but dyed for 2 min. (dull purple)
(*d*) As (*b*), but dyed for 5 min. (bluish purple)
(*e*) As (*b*), but dyed for 60 min. (full black)
(*f*) Treated as (*c*), then rinsed and boiled for 5 min. in water
(*g*) Fabric dyed in soln. of preformed water-soluble blue lake of hæmatein with K_2CrO_4

FIG. 4—Reflectance Spectra of Woollen (Flannel) Fabric mordanted with Potassium Dichromate and dyed with Hæmatein. Arrows ↑ indicate approx. position of minima in original traces

The insoluble complex molecule of logwood black must be retained in the fibre largely by the simple difficulty of dislodging it through the pores. This is a similar conclusion to that reached by Race, Rowe, and Speakman[12] regarding the retention of the chromium lakes of some synthetic mordant dyes by wool. An earlier suggestion was that the resistance of mordanted dyes to wet treatments could be attributed to some direct linkage of the mordanting metal atom with the fibre[7].

It is possible that the synthetic mordant dyes may follow a similar course of reactions with mordanting salts to those described above.

Experimental

The preparation of the pure colouring matters has been described in Part I[1].

PREPARATION AND EXAMINATION OF LAKES IN SOLUTION*

For colorimetric determinations a series of increasing amounts of 0·1% metal salt solution were added to 10-c.c. portions of 0·1% hæmatein or hæmatoxylin solution, and the solutions were boiled for 60 sec. to complete the lake formation. The solutions (all aqueous) were then diluted and measured, at the peak absorption wavelength of the lake, on the absorptiometer or spectrophotometer†.

The lakes from metals other than chromium or aluminium, or from brazilin and brazilein, were found to be too unstable in water to be examined by this method. In most cases they tend to precipitate wholly or partly as soon as formed, and the use of organic solvents or dispersing agents does not prevent this.

Tests of Sign of Ionic Charge

Two simple qualitative methods have been used to determine the sign of charge on the water-soluble lakes—(i) Examination of the effect of the solutions on anodised aluminium and powdered silica (quartz): these are positively and negatively charged in water, and are coloured only by anions and by cations respectively. (ii) Examination of the rate of spread of a drop of solution upon filter papers previously impregnated with cationic or anionic surface-active agents and dried (a method proposed by Rutter[13] for facilitating the chromatography of dyes): anionic lakes are retarded by the first and cationic lakes by the second.

An attempt was made to confirm the magnitude of the ionic charge by passage of the solutions through columns of the appropriate ion-exchange resins, followed by electrometric titration, but consistent results were not obtained in successive experiments. This may have been due to some precipitation of free acid occurring in the resin columns.

Brazilein lakes are all insufficiently water-soluble for colorimetric analysis to be applicable.

Examination of Change in pH of Lake Solutions

The blue lake was prepared by boiling for 2 min. mixed aqueous solutions of hæmatoxylin and potassium chromate in the quantities given (Fig. 3). The solutions were then corked up and allowed to stand in a thermostat tank, small samples being withdrawn at intervals, cooled, and measured with the (Marconi) glass electrode.

PREPARATION OF LAKES IN SUBSTANCE‡

Chromium (1 : 1) Complexes

(*a*) FROM HEXA-AQUOCHROMIC CHLORIDE OR CHROMIC FLUORIDE—If excess of colouring matter is present from the start, as it has been in the present preparations of lakes in substance from

* For a general survey of the chemistry of the metal chelate compounds, see Martell and Calvin[9]. Merry[10] gives an account of the chemistry of chromium salts (summarised by Giles[7]).

† A colorimetric method of a somewhat different type has been used by Job (1928) and Smith *et al.* (1940) for determining the complex ratio of soluble metal chelate compounds (see Martell and Calvin[9]).

‡ The products were not intensively dried, and it has been assumed throughout that one water molecule will remain bound (by a hydrogen bond) to each free phenolic group in the molecules. The analytical data are consistent with this assumption. The ratio of combination between a water molecule and a phenolic group is 1 : 1[2].

chromic chloride, etc., any cationic lake formed will be accompanied in the solution by gegenions consisting of inorganic and organic (i.e. colouring matter) anions. The salt formed with the latter may be less soluble than that formed with the inorganic anion, so that in the prolonged extraction process following the evaporation of the original solution it may remain and the inorganic salt may be washed away. Even if excess of colouring matter is not used, a consideration of the typical equilibria—

$$Hhn + [Cr(H_2O)_6]Cl_3 \rightleftharpoons [hnCr(H_2O)_4]Cl_2 + HCl + 2H_2O \rightleftharpoons [hnCr(OH)(H_2O)_5]Cl + 2HCl + 2H_2O$$

will show that, as the reaction mixture is concentrated, the equilibria will tend to move back towards the initial state: i.e. more hæmatein anion will be formed leading to the precipitation of more of its salt with the cationic lake. We should therefore expect to find such complex salts to be present in the final product, as indeed they appear to be.

A mixture of 2·5 g. hæmatein dissolved in 60 c.c. ethanol and either (i) 1·4 g. hexa-aquochromic chloride $CrCl_3,6H_2O$ in 30 c.c. ethanol, or (ii) 0·8 g. chromium fluoride in 50 c.c. water, was refluxed for 12–15 hr. and then evaporated to dryness. The residue was (Soxhlet-) extracted with *iso*propanol for 3 days to remove free hæmatein and chromic chloride, then warmed with a little ether to complete the removal of impurities, filtered off, and oven-dried at 100–110°C. The product was partly soluble in hot water, more so in dilute mineral acid, and dyed wool a dull purple.

Found: H 4·5, Cr 5·95 (mean of 14 preparations by different operators, range 5·4–6·8); $(C_{16}H_{11}O_6)Cr,10H_2O$ (IV*a*) requires H 4·7, Cr 4·6; $(C_{16}H_{11}O_6)_2Cr(OH),7H_2O$ (IV*b*) requires H 4·7, Cr 6·55; 30 parts of IV*a* + 70 parts of IV*b* require H 4·7, Cr 6·0%.

A brazilein lake was similarly prepared from hexa-aquochromic chloride, the colouring matter being partly in solution and partly in suspension in the solvent (ethanol). Soxhlet extraction was by Cellosolve.

Found: Cr 5·8; $(C_{16}H_{11}O_5)_2Cr,7H_2O$ (V*a*) requires Cr 5·1; $(C_{16}H_{11}O_5)_2Cr(OH),5H_2O$ (V*b*) requires Cr 7·2; 67 parts of V*a* + 33 parts of V*b* require Cr 5·75%.

A blue–black lake, probably largely in the 2 : 1 state (Found: Cr, 10·5%) was formed by treatment of 2 g. of hæmatein with 2 g. of chromic fluoride in 100 c.c. of 25% aqueous methanol at 40°C. for 15 hr.

(*b*) FROM "CHROMIC CHLORIDE TETRAHYDRATE" $[CrCl_2(H_2O)_4]Cl$—A mixture of solutions of 1·25 g. hæmatein in 80 c.c. ethanol and 0·85 g. of the chromic salt in 50 c.c. ethanol was refluxed for 24 hr. The purple mixed solution was evaporated to dryness at 40°C., and the residue (Soxhlet-) extracted for several hours with *iso*propanol until no more coloured materials passed into the extract. Finally, the material was washed with ether and dried in a vacuum desiccator. The dark purple amorphous product was partly soluble in hot water, more so in dilute acid solutions, and quite soluble in concentrated mineral acids; it was insoluble in organic solvents. The aqueous solutions coloured wool and silica purple, but did not affect anodised aluminium.

Found: Cr 12·0, 11·8; Cl present, but no Cl^- ion; $(C_{16}H_{11}O_6)CrCl_2,4H_2O$ (VI*a*) requires Cr 10·6; $(C_{16}H_{11}O_6)Cr_2(OH)_2Cl_2,7H_2O$ (VI*b*) requires Cr 15·3; 70 parts of VI*a* + 30 parts of VI*b* require Cr 12·0%.

The brazilein lake was similarly prepared, the colouring matter being only partly in solution in the reaction mixture.

Found: Cr 15·4, 15·1; $(C_{16}H_{11}O_5)CrCl_2,3H_2O$ (VII*a*) requires Cr 11·3; $(C_{16}H_{11}O_5)Cr_2Cl_2(OH)_2,6H_2O$ (VII*b*) requires Cr 16·4; 25 parts of VII*a* + 75 parts of VII*b* require Cr 15·1%.

Chromium (2 : 1) Complexes

(*a*) FROM POTASSIUM DICHROMATE—Hæmatoxylin (10 g.), dissolved in 500 c.c. water, was mixed with 3 g. potassium dichromate dissolved in 100 c.c. water, and the mixture boiled for a few minutes to precipitate the flocculent blue–black lake, which was then separated by filtration, well washed with hot water, and dried at 110°C.

One preparation was dissolved, without previous drying, in hot dilute aqueous ammonia solution, the solution was clarified with charcoal, and the complex was precipitated with dilute acetic acid.

Found:* C 46·5, H 4·2, Cr 9·2; $(C_{16}H_{11}O_6)_3(OH)_3Cr,10H_2O$ (VIII*a*: M = Cr) requires C 42·0, H 4·6, Cr 11·4; $(C_{16}H_{11}O_6)_4(OH)_3Cr_2,8H_2O$ (VIII*b*: M = Cr) requires C 52·5, H 4·25, Cr 7·10; 50 parts of VIII*a* + 50 parts of VIII*b* require C 47·3, H 4·4, Cr 9·3%.

(The complex $[hnCr(OH)_2hn]_3[Cr(H_2O)_6],12H_2O$ requires C 47·5, H 4·5, Cr 8·6%, and thus has an analysis close to that found, but we consider that olated bodies are more likely to be present.)

(*b*) FROM HEXA-AMMINOCHROMIC NITRATE—Aqueous solutions of mixtures of hæmatein and hexa-amminochromic nitrate, heated on the boiling water-bath for several hours, deposited a dark bluish-black precipitate, which was filtered off, washed well with water, and dried.

Found: Cr 9·3, 8·9, 9·1% in successive preparations; N absent.

The composition probably resembles that of the product prepared with dichromate.

(*c*) FROM POTASSIUM CHROMATE IN AQUEOUS-ALCOHOLIC SOLUTION—A solution of 1·6 g. hæmatein in 100 c.c. methanol was mixed with a solution of 0·73 g. potassium chromate in 60 c.c. water and boiled under reflux for 14 hr. The mixture was then evaporated to dryness at 40°C., finely ground, boiled under reflux with water for 18 hr., (Soxhlet) extracted with Cellosolve until the extracts were no longer coloured, washed with ether, and dried at 100–120°C. for 10 hr.

Found: Cr 8·8, 8·4; the rather low chromium analysis suggests that this product may perhaps contain some of the 1 : 1 lake.

A lake was similarly prepared from brazilein (0·95 g.) in 75 c.c. ethanol and 0·62 g. potassium chromate in 45 c.c. water, refluxed for 10 hr. Found: Cr 10·1, 9·9. Another was prepared from brazilein and potassium dichromate in aqueous solution (as above).

* The chromium analysis is the mean of several preparations (Cr 9·0–9·4%). Analysis for chromium by weighing the ash after microcombustion gave values 0·5–1·0% high compared with those given by peroxide fusion. This is attributed to the presence of a little chromium carbide in the ash. Carbon analyses are therefore correspondingly corrected.

Found: Cr 12·8; $(C_{15}H_{11}O_6)Cr_2O_7,5H_2O$ (IX*a*) requires Cr 24·5; $(C_{15}H_{11}O_6)_3Cr_2(OH)_3,8H_2O$(IX*b*) requires Cr 12·3; $(C_{15}H_{11}O_6)_4Cr(OH)_3,4H_2O$ (IX*c*) requires Cr 7·8%.

The lakes actually obtained are probably mixtures of IX*c* with products closely resembling IX*a* and IX*b*.

Cobalt Lakes from Hexa-amminocobaltic Chloride

This compound $[Co(NH_3)_6]Cl_3$, has been used by Morgan *et al.*[11] because of the ease with which it differentiates between lake- and salt-forming groups in a molecule. Hæmatein (2·3 g.) was pasted with Cellosolve, then dissolved in 75 c.c. of hot water, and the solution added to 3·0 g. of hexa-amminocobaltic chloride in 25 c.c. of warm water. On refluxing on the boiling water-bath for 24 hr. and cooling, a bluish precipitate settled, leaving a clear supernatant liquor. The precipitate was filtered off and washed with warm water until no yellowish tinge was observed in the filtrate, then dried. Yield 4 g. The product was insoluble in water and organic solvents, but it was very slightly soluble in dilute sulphuric acid.

Found: N 11·9, Co 14·8; $(C_{15}H_{12}O_6)_3(C_{15}H_{11}O_6)Co_3$, $12NH_3,4H_2O$ (X*a*) requires N 12·5, Co 13·1; $(C_{15}H_9O_6)_3(OH)Co_{7/2}$, 7½ NH_3,2½ H_2O (X*b*) requires N 11·8, Co 15·2; 10 parts of X*a* + 90 parts X*b* require N 11·85, Co 15·0%*.

A lake was similarly prepared from brazilein.

Found: N 6·8, Co 11·3; $(C_{15}H_{11}O_5)_3Co,2NH_3,3H_2O$ (XI*a*) requires N 2·85, Co 5·95; $(C_{15}H_{10}O_5)_3(OH)Co_{5/2}$, 4½$NH_3$,1½$H_2O$ (XI*b*) requires N 7·8, Co 12·7; 20 parts of XI*a* + 80 parts of XI*b* require N 6·8, Co 11·4%*.

Copper Lakes

Solutions of 1 g. hæmatein in 75 c.c. ethanol and 0·25 g. cupric sulphate crystals in 25 c.c. water were mixed and boiled under reflux for 15 hr. The liquor was then evaporated to dryness at 40°c., and the residue first repeatedly washed with aqueous ethanol, refluxed with aqueous ethanol for 9 hr., and then dried in a vacuum desiccator. The product was insoluble in water and organic solvents. In concentrated sulphuric acid it gave a deep red solution, and in 10% aqueous potassium hydroxide a reddish-blue solution. Hot suspensions of the lake coloured both anodised aluminium and silica on standing.

Found: Cu 15·25; $(C_{15}H_{11}O_6)_2Cu_3,6H_2O$ (XII) requires Cu 15·4%.

A second preparation, using 1 g. hæmatein and 0·5 g. (i.e. excess) cupric sulphate, gave the following analysis—

Found: Cu 11·1, 10·9 (volumetrically), 11·2 (by combustion), C 42·65, H 4·05; SO_4 absent.

The material was possibly a mixture of cuprous and cupric lakes with some metal oxide or hydroxide.

A brazilein lake was similarly prepared, using 0·6 g. cupric sulphate in 40 c.c. water, and refluxing for 13 hr. Subsequent washing was with hot water, followed by refluxing for 5 hr. with methanol. Found: Cu 11·35, 11·5 (volumetrically); 12·5 (by combustion); C 46·1, H 3·95; this may also contain oxide or hydroxide. A product from 1 g. brazilein and 0·25 g. cupric sulphate gave Cu 17·6%. This is considerably higher than the lake corresponding to XII and probably also represents a content of initial hydroxide, etc.

Iron Lakes

(*a*) Hæmatoxylin (1·1 g.), dissolved in 40 c.c. water, was mixed with ferric ammonium sulphate (0·65 g.) dissolved in 30 c.c. water and boiled under reflux for 6 hr. The mixture was then evaporated to dryness at 40°c., well washed with hot water, refluxed with aqueous ethanol for several hours, then separated by filtration, washed with aqueous ethanol, and dried in a vacuum desiccator. An aqueous suspension coloured anodised aluminium, but not silica. Found: Fe 9·0, 9·25.

(*b*) A solution of hæmatein (0·5 g.) in 40 c.c. methanol was mixed with a solution of 0·32 g. ferric ammonium sulphate in 20 c.c. water and boiled under reflux for 15 hr. The mixture was then evaporated to dryness at 40°c., repeatedly washed with hot water, refluxed with aqueous Cellosolve (6 hr.), washed with water, then ether, and dried at 100°c. An aqueous suspension did not colour either anodised aluminium or silica. Found: Fe 9·2%.

(*c*) Brazilein (1 g.), dissolved in a mixture of 25 c.c. Cellosolve and 50 c.c. water, was mixed with a solution of 0·75 g. ferric ammonium alum in 40 c.c. water and boiled under reflux for 16 hr. The mixture was evaporated to dryness at 50°c., and the residue repeatedly washed with boiling water and then boiled under reflux for 13 hr. with aqueous ethanol. It was filtered off, washed with hot water, then with methanol and finally with ether, and dried in a vacuum desiccator. A second preparation was purified by refluxing first with water, then with Cellosolve. Found: Fe 9·1, 9·15 (in different preparations). All these iron lakes must be mixtures of similar constitution to the corresponding lakes from chromium, i.e. VIII*a* + VIII*b*, IX*a* + IX*b* (M = Fe).

Tin Lake

Hæmatein (1·52 g.) dissolved in methanol (80 c.c.) was mixed with stannous chloride (0·72 g.), dissolved in 40 c.c. water containing a little hydrochloric acid, and boiled under reflux for 25 hr. The lake, which had precipitated, was separated by filtration, well washed with hot dilute hydrochloric acid to remove unchanged tin salt, then (Soxhlet-) extracted for several days with ethanol to remove unchanged hæmatein, and finally washed with ether and dried in a vacuum desiccator. The brazilein lake was similarly prepared. Both these compounds gave very considerably higher analyses for tin (ca. 40%) than could normally be accounted for. It is assumed they were contaminated with basic inorganic tin salts.

DETERMINATION OF METALS IN LAKES

Chromium

Besides the weighing of the ash after micro-combustion in oxygen, the following methods were

* Morgan and Smith[11] observed that when a hexa-amminocobaltic salt is used for lake formation, only one-third of the unchelated monobasic acidic groups in the molecule (including in certain cases isolated phenolic groups) are substituted by the $[Co(NH_3)_6]$ group. Presumably the remaining two-thirds serve to neutralise the two positive charges associated with this group. Consequently it has been assumed here that the unchelated phenolic groups in brazilein and hæmatein behave in this way. The ammonia liberated from combination with cobalt will produce an alkaline environment and thus ensure ionisation of phenolic groups.

used to determine chromium—(*a*) A known weight of lake was fused with sodium peroxide in a nickel crucible. The mass, after cooling, was leached out with boiling water, and the solution filtered, boiled to remove oxygen, and acidified with hydrochloric acid to convert chromate to dichromate. The solution was then diluted to a given volume; to an aliquot portion a little concentrated hydrochloric acid was added, followed by potassium iodide crystals, and the liberated iodine was titrated with 0·1 N. sodium thiosulphate solution, using starch indicator. The accuracy of the method was checked by determination of a known chromium salt.

(*b*) Ashing in a platinum crucible gave high values, presumably because of incomplete combustion or carbide formation. Better values were obtained if the crucible was allowed to cool from time to time and the ash moistened with a few c.c. of ethanol.

Cobalt

This was determined by the thiocyanate-pyridine method[15].

Copper and Iron

The lake (0·05 g.) was ignited to constant weight in a porcelain crucible, the residue cooled, 10 c.c. sulphuric acid (sp. gr. 1·84) added, and the mixture carefully stirred into 100 c.c. cold water; 25-c.c. aliquot portions of the solution were then titrated with 0·1 N. sodium thiosulphate solution, after addition of ca. 3 g. potassium iodide crystals, using starch indicator. For the iron analysis, a small quantity of a suspension of cuprous iodide was also added to the mixture before titration. Copper was also determined by direct weighing of the ash after microcombustion in oxygen.

PHYSICAL ANALYSES

Spectrophotometric measurements of solutions were made on a Unicam SP 500 photoelectric spectrophotometer, and absorptiometric determinations on either a Hilger Spekker or an E.E.L. photoelectric absorptiometer. The reflectance spectra of dyed fabrics were obtained on a Hardy automatic recording spectrophotometer, by measurement against magnesium oxide, using a double fabric layer with a matt black backing.

ATTEMPTED PREPARATIONS OF MODEL POLYHYDROXY- AND HYDROXY-QUINONE COMPOUNDS

The following are brief details of some attempted syntheses—

(*a*) *4 : 4′-Dihydroxydiphenylmethane*[6]

Condensation of aniline with formaldehyde to give methylenediphenyldiimide; rearrangement (in presence of aniline hydrochloride) to give 4 : 4′-diaminodiphenylmethane; tetrazotisation and boiling with water. Colourless crystals, m.p. 158°C.

(*b*) *4 : 4′-Dihydroxy-α-methyldiphenylmethane*

Condensation of phenol with paraldehyde in presence of concentrated hydrochloric acid. Colourless crystals, m.p. 122°C.

(*c*) *4 : 4′-Dihydroxytriphenylmethane*

Condensation of phenol with benzaldehyde (in presence of sulphuric acid), followed by removal of acid with cold water, phenol by steam distillation and resins with benzene, then crystallisation from dilute acetic acid and finally ethanol. Colourless crystals, m.p. 160°C.

(*d*) *3 : 4 : 4′-Trihydroxybenzophenone*

(i) The following condensations were attempted without success—catechol with *p*-hydroxybenzoic acid (in presence of anhydrous zinc chloride), with *p*-nitrobenzoic acid (+ phosphoryl chloride or aluminium chloride), or with *p*-nitrobenzoyl chloride (+ aluminium chloride).

(ii) An attempted rearrangement of catechol di-*p*-nitrobenzoate (in nitrobenzene with aluminium chloride) to a benzophenone derivative was unsuccessful.

(iii) Demethylation of the condensation product of veratrole and anisoyl chloride[8] (by hydriodic acid, aluminium chloride in carbon disulphide or nitrobenzene, or pyridine hydrochloride at 220°C.), was only partly successful, the products being uncrystallisable oily mixtures.

(*e*) *3 : 4 : 3′ : 4′-Tetrahydroxybenzophenone*

Condensation of protocatechuic acid with catechol in presence of anhydrous zinc chloride gave a substance with m.p. 209°C., after recrystallisation from water. This was not further investigated.

(*f*) *3 : 4 : 3′ : 4′-Tetrahydroxydiphenylmethane (and its α-Methyl Derivative)*

(i) Condensation of catechol with formaldehyde or paraldehyde or of guiacol with paraldehyde. These methods produced resinous materials.

(ii) Treatment of catechol and protocatechuic acid with anhydrous zinc chloride at 160°C. No condensation took place.

(iii) Treatment of *o*-nitrophenol and acetaldehyde with mineral acid. No condensation took place.

(iv) Treatment of *o*-nitroaniline with formaldehyde, followed by reduction. Only *o*-phenylenediamine was obtained.

(*g*) *3 : 4 : 3′ : 4′-Tetrahydroxytriphenylmethane*

(i) Condensation of catechol or guaiacol with benzaldehyde produced resins.

(ii) An attempted condensation of *o*-nitrophenol with benzaldehyde was unsuccessful.

OXIDATION OF *pp′*-DIHYDROXY COMPOUNDS

When treated with solutions of diazotised aniline or sulphanilic acid, 4:4′-dihydroxydiphenylmethane and its α-methyl derivative did not react: 4:4′-dihydroxytriphenylmethane, however, was oxidised, with evolution of nitrogen, to a red amorphous compound, apparently a *p*-quinone. No azo compound appeared to be formed. (Hæmatoxylin behaves similarly)[5]. Alkaline hydrogen peroxide likewise did not affect the diphenylmethane compounds, but oxidised the triphenylmethane compound to the red product. Attachment of the central carbon atom to either an aromatic nucleus, or a heterocyclic ring and a reduced ring (as in hæmatoxylin), therefore renders the compound more susceptible to oxidation.

The present and preceding papers summarise a number of researches carried out in this laboratory over the period 1946–1954, in which the following have also assisted—Messrs. E. N. Farquharson, S. Gallagher, J. Harper, E. L. Neustädter, and I. S. Shaw, whom we therefore wish to thank. We also thank Dr. (late Professor) W. M. Cumming and Professor P. D. Ritchie for their continued interest and encouragement and many helpful suggestions; also British Celanese Ltd. (Derby), the British Dyewood Co. Ltd. (Glasgow), together with the West Indies Chemical Co. Ltd. and the Yorkshire Dyeware & Chemical Co. Ltd.; British Nylon Spinners Ltd. (Pontypool), Clayton, Metcalfe & Co. Ltd. (Halifax), and the British Wool Section of the Ministry of Agriculture and Fisheries (Bradford) for the gift of cellulose acetate, samples of logwood products, nylon, silk, and wool respectively; Mr. G. Baxter for the spectrophotometric analysis of solutions; Mr. A. Ogilvie for making the dielectric constant measurements; Dr. A. B. Crawford for helpful discussions; and Dr. R. H. Peters and Imperial Chemical Industries Ltd., Dyestuffs Division (Manchester), for the spectrophotometric measurements on dyed fabrics. A Hilger Spekker photoelectric absorptiometer was lent by Imperial Chemical Industries Ltd., Central Research Department (London). Micro-analyses were by Dr. A. C. Syme, Royal Technical College, Glasgow, and by Drs. Weiler and Strauss, Oxford. One of us (J. N. D.) is indebted to the Government of India for financial assistance.

APPENDIX

Metal Lakes of Brazilein and Hæmatein*

The following are the structures which most nearly accord with the elementary analyses and properties of the solid products obtained—

CHROMIUM (1 : 1) COMPLEXES

From Hexa-aquochromic Chloride

IV*a* $[hn\ Cr\ (H_2O)_4]^{3+}2[hn]^-6H_2O$ (30)

IV*b* $[hn\ Cr\ (OH)\ (H_2O)_3]^+[\ hn]^-4H_2O$ (70)

V*a* $[bn\ Cr\ (H_2O)_4]^{3+}2[bn]^-3H_2O$ (67)

V*b* $[bn\ Cr\ (OH)\ (H_2O)_3]^+[bn]^-2H_2O$ (33)

From Tetra-aquodichlorochromic Chloride

VI*a* $[hnCrCl_2(H_2O)_2]2H_2O$ (70)

VI*b* $[hnCrCl(H_2O)_3]^+[CrCl_2(OH)_2(H_2O)_2]^-2H_2O$ (30)

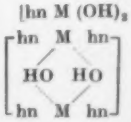
VII*a* $[bnCrCl_2(H_2O)_2]H_2O$ (25)

VII*b* $[bnCrCl(H_2O)_3]^+[CrCl_2(OH)_2(H_2O)_2]^-H_2O$ (75)

COMPLEXES FORMED FROM CHROMATES, DICHROMATES, AND FERRIC AMMONIUM SULPHATE

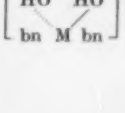
(M = Cr or Fe)

VIII*a* $[hn\ M\ (OH)_2\ hn]\ [M(OH)(H_2O)_4]^+4H_2O$

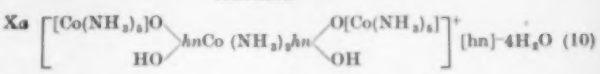
VIII*b*  $8H_2O$

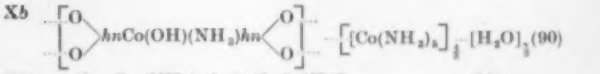
IX*a* $[bn\ Cr\ (H_2O)_4]^{3+}[Cr_2O_7]^{3-}H_2O$

IX*b* $[bn\ M(OH)_2\ bn]^-[M(OH)_2(H_2O)_4]^+2H_2O$

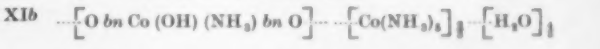
IX*c*  $4H_2O$

COMPLEXES PREPARED FROM HEXA-AMMINOCOBALTIC CHLORIDE

X*a*  (10)

X*b*  (90)

XI*a* $[bn\ Co\ (NH_3)_2\ bn]^+\ [bn]^-3H_2O$ (20)

XI*b* 

COMPLEX PREPARED FROM CUPRIC SULPHATE

XII $[Cu(H_2O)_2{=}hn{=}Cu(H_2O)_2]^+[hn]^-2H_2O$

XIII—Suggested Formulation of the Oiated Logwood Black–Chromium Complex

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bn, *hn* = Corresponding dibasic and tribasic anions respectively.
Figures in brackets show probable percentages of components in the samples examined.

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CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Colour Changes of Vat Dyeings during Soaping

On the strength of considerable evidence, I advanced a molecular theory to explain the colour changes observed in vat dyeings, suggesting that this phenomenon was due to changes in the degree of polarisation of the dye molecules [1].

This theory runs counter to the opinion that colour change is to be attributed to the state of aggregation of the dye (amorphous or crystalline) and has given rise to considerable discussion [2]. However, I shall confine my remarks to the comments recently made in your *Journal* [3,4].

I would submit that H. Sumner and T. Vickerstaff's measurements [3] of the soaped Caledon Yellow 3G (ICI) dyeing show positive and not negative dichroism, because they used regenerated cellulose film as the substrate, and not ramie fibre, as I did. It has been established that, whereas ramie fibres show negative dichroism, regenerated cellulose shows positive dichroism.

This interesting example is an indication that certain dyes are incorporated differently in native and in regenerated cellulose fibres, and is by no means an isolated case.

The individual behaviour and differences in fastness shown by certain dyes on cotton and viscose rayon is a well known but little understood phenomenon. In the case of Caledon Yellow 3G, it is not very probable that in one case the crystals run parallel to the fibre axis, and in another perpendicular to it.

Caledon Yellow 3G is not the only example to demonstrate the lack of agreement between dichroism in the crystal and in the soaped fibre. Many other examples could be given, e.g. Ciba Blue 2B and Caledon Red 5G, the latter showing positive dichroism in the crystal, whilst its soaped dyeings on ramie exhibit negative dichroism. Measurements indicate that, in this case, the dichroism is negative also on the viscose film, which is at variance with the findings of H. Sumner, T. Vickerstaff, and E. H. Waters [5], which indicate positive dichroism.

As it is, it appears to me that this excellent paper [5] entirely supports the molecular theory, since the writers state that neither the electron microscope nor X-ray analysis give any indications of crystallisation in the fibre as the result of soaping at the boil.

I cannot accept the evidence offered by the analogous behaviour observed during the ageing of colloidal suspensions of vat dyes as proof, since whether or not (assuming the same particle size) the colour of the unsoaped or that of the soaped dyeing results depends entirely on the experimental conditions (temperature, alkaline or acid peroxide solution, type of dispersing agent) and the constitution of the dye used.

In reply to E. Kornreich [4], I regret that I cannot subscribe to the crystallisation theory but must insist on the molecular theory. I cannot understand why Kornreich stated that my findings did not contradict the opinion expressed in his paper. I also feel that he was not justified in saying that I had not made sufficient reference to his work, particularly as he has introduced nothing essentially new as compared with the papers of R. Haller, P. Bean and F. M. Rowe, and notably E. I. Valkó. We are in complete disagreement as to the necessity for new theories on an issue which Kornreich claims to be already settled.

The phenomenon of colour changes of vat dyes is by no means fully understood, and even the molecular theory is nothing more than a new hypothesis which may serve as a basis for further investigations. To what extent differences in polarity actually exist, and to what degree isomerism (monomers and dimers, *cis* and *trans* forms, etc.) is either partly or exclusively involved, are questions which had to remain unanswered.

Any new theory which may contribute to a better understanding of these problems should, therefore, be welcomed, and the merits or demerits of the molecular theory of colour change will be judged not by theoretical discussion but by the extent to which it will eventually advance the science of dyeing.

J. WEGMANN

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SWITZERLAND

16th July 1954

[1] Wegmann, J., *Textil-Rund.*, **8**, 4, 97, 157 (1953).
[2] Müller, J., *ibid.*, **8**, 622 (1953).
[3] Sumner, H., and Vickerstaff, T., J.S.D.C., **70**, 123 (March 1954).
[4] Kornreich, E., *ibid.*, **70**, 238 (June 1954).
[5] Sumner, H., Vickerstaff, T., and Waters, E., *ibid.*, **69**, 181 (1953).

It would appear that there is full agreement between Dr. Wegmann and myself about the colour change phenomena not being due to aggregation but to changes in the orientation of the dye molecules. The disagreement concerns whether this change is due to crystallisation or polarisation. If crystallisation is regarded as rearrangement of the dye aggregates in orderly fashion on the molecular level—and this was the essence of my paper—the disagreement almost resolves itself.

Dr. Wegmann is, however, not justified in saying that I had introduced nothing essentially new as compared with the papers of R. Haller and of P. Bean and F. M. Rowe. In fact, my own work has shown that the view of those authors that the colour change on soaping is due to aggregation can no longer be upheld. When they referred to crystallisation they merely meant to show how far aggregation can go in forming microscopic crystals. There is to my knowledge not a single sentence in any of their publications which ascribes the colour change to the transition of the dye particles from the amorphous (disoriented) to the crystalline (oriented) state, as I have shown to be the case. As far as Valkó's paper is concerned, this was published when my work was almost completed, and it can be regarded as supporting my own views.

I trust that this puts the whole question into the right perspective, but I should be pleased to discuss any further points with Dr. Wegmann in private in order not to take up more of your valuable space.

E. Kornreich

63 Dollis Park
London N.3
26th July 1954

Notes

Proceedings of the Council

At meetings of the Council held in the Board Room of the Dyers and Finishers Association, Commerce House, Cheapside, Bradford, on 16th June and 2nd July 1954, and at the Victoria Hotel, Bradford, on 14th July 1954, the proceedings included the following items of interest—

Joint Conference—The President reported that generally it was considered that the Conference held at Scarborough during Whitsun week had proved a very happy and successful event. The cordial relationship with the Textile Institute was very pleasing.

Membership—Twenty-two applications for membership were approved. Mr. P. Buthaway was readmitted to membership.

Dyers and Finishers Association—It was agreed that a letter of thanks be sent to the Association, expressing the appreciation of the Council for the use of their Board Room.

London Section—Note was taken of a letter from the London Section mentioning the excellent work done on behalf of the Section by its former Honorary Secretary, Dr. H. W. Ellis. An amendment to the Byelaws of the London Section was approved.

Professor C. S. Whewell—Congratulations had been conveyed to Professor Whewell on his appointment to the Chair of Textile Technology in the University of Leeds.

The Late Mr. F. L. Goodall—Letters of sympathy were read, and also two cables, from the Society of Dyers and Colourists of Australia and the Dyers and Finishers Association of South Africa respectively. It was decided to send letters of condolence to Mrs. F. L. Goodall and to the Geigy Company Ltd.

Investiture of President—Mr. H. H. Bowen (*Past President*) invested Mr. Fred Smith with the Presidential Badge.

Chairman of Council—Mr. Fred Smith was elected Chairman.

Venue—It was resolved that in future Council meetings be held in the Victoria Hotel, Bradford.

Meetings of Council and Committees

August

Council—No meeting

Publications—17th

Colour Index Editorial Panel—26th

Death

We regret to report the loss by death of Mr. G. H. Schuler. As Chairman of the AATCC Publicity Committee, and Secretary of their *Colour Index* Editing and Marketing Committees, Mr. Schuler had played a prominent part in making the business and other arrangements necessary for the production of the Second Edition of the *Colour Index*, and had been extremely helpful in direct correspondence with the Society.

Colour and Textiles

Joint Conference held at Scarborough

The Proceedings of the Conference on "Colour and Textiles", held at Scarborough on 8–11th June 1954 under the joint auspices of the Society and the Textile Institute, have been published as a separate volume, which contains both lectures and discussions. A copy has been sent to every member of the Society. Additional copies may be purchased at 17s. 6d. each, post free, from the Society of Dyers and Colourists, 19 Piccadilly, Bradford 1, Yorkshire.

New Books and Publications

Annual Reports on the Progress of Chemistry for 1953

Volume L

London: The Chemical Society. 1954. Pp. 430. Price, 30s. 0d.

This issue is the Jubilee Number and covers five chapters which contain 4212 references, many of them composite.

Section I on *General and Physical Chemistry* is set out in five subsections with 913 references, which deal respectively with molecular spectra, thermochemistry, chemical change in homogeneous systems, reactions at solid interfaces, and the theory of liquids and liquid mixtures. It is to be noted that much effort has been directed to the more precise determination of molecular dimensions, and that a study in detail of an ultraviolet band system of benzene indicates that the molecule contains three-electron C–C bonds. Several investigations involving the exchange of sulphur have been made, and that of ^{35}S between the diethyl polysulphides indicates that exchange occurs only with sulphur atoms not attached to carbon.

Section II on *Inorganic Chemistry*, with 359 references, notes progress in the quantitative interpretation of the relative stabilities of metal complexes, in the chemistry of nitrogen, phosphorus, and sulphur (especially the discovery of the blue unstable compound "imine" (NH) and of the new allotropes, brown phosphorus and both purple and green sulphur), and in the preparation of metal *cyclo*pentadienyls and of carbonyls, which are now of much industrial importance, e.g. in connection with hydroformylation and carbonylation reactions.

Section III on *Organic Chemistry* contains 1477 references, which are included in its eight subsections on theoretical organic chemistry, stereochemistry, general methods, aliphatic, homocyclic, and heterocyclic compounds, carbohydrates, and peptides, proteins, and amino acids. A noteworthy feature of the year under review has been the appearance of at least eight books (named) which have greatly clarified modern viewpoints in regard to theoretical aspects of organic chemistry. The calculation by molecular-orbital methods of reactivities in the various possible positions in aromatic systems continues to arouse interest. For example, when an unsaturated substituent such as vinyl, phenyl, or butadienyl orients substitution in the benzene nucleus, the *ortho* should be more reactive than the *para* position; that *para* substitution is actually favoured experimentally, as in the nitration of diphenyl, is attributed by some authors to steric hindrance of *ortho* substitution, and by others to the fact that the quinonoid transition state for *para* substitution will be energetically more favourable than for *ortho* substitution. The rate of nitration, catalysed by nitrous acid, of *p*-chloroanisole in acetic acid appears to be controlled by nitrosation, the entities NO^+ and N_2O_4 both being concerned in the reaction. Electrophilic *N*-nitrosation is shown to be kinetically rate-determining in the diazotisation of aromatic amines in dilute aqueous solution; in the absence of nucleophilic anions, the operative nitrosating agents are N_2O_3 and $H_2NO_2^+$, whereas when such ions as Cl^- are added to the solution, the reaction may be diverted through such entities as NOCl. Until recently, the most convincing demonstrations of the importance in chemical reactions of C–H hyperconjugation have come from reactions facilitated by electron-releasing groups, but clear examples are now cited in the field of nucleophilic aromatic substitution. Oxidations of naphthalene, benzoic acid, and phthalic acid by Fenton's reagent, and by hydrogen peroxide activated by ultraviolet radiation, show that naphthalene forms *α*- and *β*-naphthol in the ratio 3·8 : 1, but does not give the dihydro-diols which are formed in biological oxidations. Further oxidation gives hydroxybenzoic acids from all these compounds; the *ortho* : *meta* : *para* ratio from naphthalene oxidation is 10 : 5 : 2 and from benzoic acid oxidation is 10 : 5 : 5, data which differ considerably from those in previous reports. A study of the photosensitised oxidation of alcohols indicates that radicals formed from quinonoid dyes can initiate reaction by dehydrogenation. In the two years that have elapsed since stereochemistry was last reviewed, much significant work has appeared, and the importance of modern ideas concerning the conformations of cyclic compounds is evident in recent work on homocyclic compounds, including steroids, and in carbohydrate chemistry. Evidence that the valency bond joining alkyl substituents to an aromatic molecule (normally rigidly set in the plane of the nucleus) can depart from coplanarity in some polynuclear aromatic systems is accumulating. Still more hydrocarbons have been obtained from the higher-boiling fractions of coal-tar distillation products, and include 1-phenylnaphthalene, 9:10-dihydroanthracene, 10:11- and 11:12-benzofluoranthene, and benzo[*mno*]fluoranthene, which was synthesised only recently; coronene has been isolated from the oil produced by hydrogenation of coal, and 4-methyl- and 4:9-dimethyl-pyrene have been found among the products of high-pressure petrol synthesis. The significance of the pollution of city atmospheres by polycyclic aromatic hydrocarbons has been stressed, and anthracene, pyrene, fluoranthene, 1:2-benzopyrene, the highly carcinogenic 3:4-benzopyrene, perylene, and 1:12-benzoperylene have been detected in the air of Salford. It has been found that aromatic hydrocarbons whose structures cannot be written in terms of Kekulé structures are exceedingly unstable. Certain aspects of anthraquinone chemistry, particularly with regard to dyes, have been reviewed, and the use of polyphosphoric acid to cyclise *o*-benzoylbenzoic acids to anthraquinones has been strongly recommended. The uncertainty regarding the orientation of the dibromoanthanthrone obtained by direct bromination of the quinone has been

removed by proof that it is the 4:10-derivative. Halogen atoms may be removed from halogeno-nitro compounds by heating with benzoic acid and copper; chlorine and bromine are eliminated only when *ortho* and *para* to nitro groups, iodine from any position, and fluorine not at all; the method has preparative possibilities. A good general method for oxidising the amino to the nitro group is lacking, but the gap appears to be filled by the use of a promising new reagent, viz. hydrogen peroxide in trifluoroacetic acid. To fill the need for methods to indicate the positions of sugars on chromatograms, several new reagents have been developed and known reagents have been made more specific; e.g. a quantitative technique using benzidine in acetic acid is satisfactory for most common sugars and their methylated derivatives except ketones, and a slightly alkaline methanolic solution of sodium borate and phenol red gives good definition with dihydroxyacetone, various pentoses, hexoses, and disaccharides, and a number of polyols. The biogenesis of porphyrins has been considerably clarified, a chemical synthesis of sucrose has been announced, and one of the greatest achievements in peptide chemistry has been accomplished, viz. the elucidation of the structure and the synthesis of oxytocin.

Section IV on *Biochemistry* reviews the four fields of extremely active research (575 references) in transfructosylation, enzymic degradation of starch and glycogen, fatty acid metabolism in animal tissues, and the constituents of marine algae.

Section V on *Analytical Chemistry* contains 888 references to work largely based on previous discoveries.

Comprehensive author and subject indexes complete a volume which will inform and stimulate the ever increasing number of workers in the various fields of chemistry.

H. H. Hodgson

Textilhilfsmittel und Waschrohstoffe

By K. Lindner. Pp. xxiv + 976. Stuttgart: Wissenschaftliche Verlagsgesellschaft m.b.H. 1954. Price, DM 113.00.

In this large volume the author expounds the chemistry, technology, and application of textile auxiliary products and of raw materials for washing and laundering agents. Such products were formerly predominantly composed of vegetable and animal oils and fats, but since about 1930 a rapid development took place, and surface-active agents and textile, laundering, and finishing products now comprise aliphatic and cyclic hydrocarbons, alcohols, phenols, ketones, carboxylic acids, fatty acids and alcohols of high molecular weight, and many other organic materials. Their chemistry is dealt with in Part I (pp. 3–292). Part II (pp. 295–589) concerns the methods of production and the properties of surface-active agents of the anion-active, non-ionic, cation-active and ampholytic types. This section ends with a description of the sulphonation technique and the newer methods of continuous sulphonation. It would have been preferable if the author could have been more selective in the manufacturing processes he describes and had given an indication of their relative value and usefulness. In Part III (pp. 593–813) the author and his collaborators describe the application of textile auxiliary products in sizing and desizing, in bleaching, dyeing, printing, and finishing, and in other textile processing methods. Dr. M. Kehren contributes an article on the oiling of wool and Dr. O. Uhl on domestic and industrial laundering. In a description of older and newer methods of raw wool scouring (written by Dr. Kehren) one misses any reference to the solvent scouring method (as practised in the U.S.A.), and nothing is said on the effect of detergents in sewage purification, a problem which has caused some interest, not to say alarm, in this country, and about which a number of investigations have been published (e.g. Sperry, *Sewage and Industrial Wastes*, **23**, 1469 (1951); Elton *et al.*, *Inst. Sewage Purification J. & Proc.*, 351 (1949); and Goldthorpe and Nixon, *J. Royal Sanitary Inst.*, **70**, 116 (1950)). To the references on laundering the book by W. W. Niven, *Fundamentals of Detergency* (New York, 1950) should be added. Part IV, written by Dr. H. Stüpel and Dr. A. von Segesser, discusses methods for testing and evaluating surface-active agents and synthetic detergents.

The author was originally asked to publish a new edition of Herbig's *Die Öle und Fette in der Textilindustrie*, last published in 1929, and the book Dr. Lindner now presents must be the result of long research and study; he has also closely read the German and foreign literature, particularly English and American, and quotes innumerable references, which are all listed at the end of the book. A catalogue of firms and products refers to firms in Germany, Austria, and Switzerland; only a few English firms are listed in another table. There are 207 illustrations and 128 tables within the text. It is a good and important book, rather lengthy in parts, but well planned and produced.

Of some interest are Dr. Lindner's views on the question of "Soap or Synthetics"; he predicts (p. 305) the "peaceful co-existence" of soap and synthetic detergents for some years to come. He agrees that for certain processes soap will continue to be used, but he thinks that synthetics derived from petroleum by-products or from paraffin products by the Fischer-Tropsch synthesis will be manufactured soon at a lower price than soap products, so that the future development of synthetic detergents depends not only on the solution of technical problems but also on economic factors.

A. F. Kertess

Handbook of Colorimetric Chemical Analytical Methods

for Industrial Research and Clinical Laboratories developed for use with the Lovibond Comparator

Pp. 119. Salisbury: The Tintometer Ltd. 1953. Price, 15s. 0d.

This book is a guide to the application of the Lovibond comparator in an analytical laboratory. It contains detailed working instructions for the

colorimetric determination of pH and of more than fifty inorganic and organic estimations in the field of chemical and clinical analysis, each ending in a colorimetric comparison. For each estimation described there is available a Lovibond disc which presents in permanent and unalterable glass a series of matchings of the colour produced under the conditions of the test by a given amount of the substance concerned.

F. F. Elsworth

Fibre Science

Edited by J. M. Preston. 2nd edition 1953. Pp. xix + 421. Manchester: The Textile Institute. Price, 40s. 0d.

The new edition of this valuable reference book on the physics and chemistry of natural and synthetic fibres has been much improved by the incorporation of new subject matter. Particular reference should be made to the chapter on protein fibres, which has virtually been rewritten to include the latest views on the molecular configuration of such fibres. Recent advances in the chemistry and properties of fibre-forming synthetic polymers, with particular reference to the inter-relation between rubbers, plastics, and fibres, and new work on the structure of the cell wall in plants have been included in the appropriate chapters. Some fine electron photomicrographs of the lamellæ of the cell wall of *Valonia* are illustrated. The inclusion of an author index as well as a subject index has improved its value for reference purposes, whilst the use of heavy type for structural formulæ combined with an overall greater clarity of printing enhances its presentation. This enlarged edition, which is about 25% longer than the first edition, will prove of great value to all workers in the textile industry.

P. W. Carlene

Paper Chromatography

By Friedrich Cramer, translated by L. Richards. 2nd edition (revised and enlarged) 1954. Pp. xii + 124 + 68 Fig. + 4 plates + 2 keys + 1 folding plate. London: Macmillan & Co. Ltd. Price, 25s. 0d.

In 1941 experimental science received a great stimulus from the invention of partition chromatography by Martin and Synge, which they described as "a new form of chromatogram depending on the partition of solutes between two liquid phases". The new technique advanced significantly in 1944 with the development of the paper partition chromatogram by Consden, Gordon, and Martin. Its elegant simplicity and tremendous potentialities soon captured the imaginations of scientists the world over, as evidenced by the hundreds of papers describing its applications which have appeared in scientific literature during the past ten years. In writing his book Dr. Cramer has realised the enormous task which faces anyone who attempts to give a comprehensive account of all this work, and has restricted himself to the production of a laboratory manual on paper chromatography. Let it be said immediately that as such this book is first class and can be thoroughly recommended to anyone who uses paper chromatography in his research or is contemplating doing so.

The book is divided into two sections. The first, and shorter, of the two commences with a brief historical introduction, and an outline of the general technique, theory, and scope of paper chromatography. Explanations are then given concerning the variety of paper-chromatographic methods used, the amounts of substances that can be conveniently separated, their detection and identification on the chromatogram, and the general methods employed for their estimation. The chromatographic qualities of various grades of filter paper are discussed, and details given for the purification of the common developing solvents. The section concludes with an account of paper electrophoresis, a technique that has been shown to give separations of protein mixtures comparable with those obtained by use of the Tiselius apparatus. It is a tribute to the author's concise expression, and no doubt to his translator's English, as well as to the clarity of his diagrams, of which no fewer than fifty-four appear in this section, that he has compressed all the essential practical procedures and pitfalls of paper chromatography into such small compass.

The second section deals specifically with the chromatographic separation, identification, and estimation of amino acids, peptides, sugars, alcohols, vitamins, purines, nucleosides, phenols, organic acids and bases, porphyrins, sterols, and other classes of organic compounds. The paper chromatography of inorganic cations and anions is also outlined. Tables of R_f values of all these substances are given, in some cases for many different solvents, and the text is well illustrated by diagrams, four colour plates, and one folding plate showing the Dent map of amino-acid spots obtained by two-dimensional chromatography. Reference is made here to Sanger's work on the determination of the amino-acid sequences in part of the insulin molecule, which furnishes an outstanding example of what can be achieved by the skilled use of paper chromatograms.

The book is well indexed and has a large, but by no means exhaustive, bibliography. Unfortunately there are typographical errors, and several well known names in the bibliography are mis-spelled. In one case an author's name has been included in the title of a journal, and some abbreviations of journal titles are non-standard. The translation is on the whole well done, but retains traces of the original German. Thus, the words "enzymatic" and "fermentative" have been used synonymously and indiscriminately, and "sec. Na phosphate" is scarcely familiar to English readers as Na_2HPO_4. Although these blemishes may cause minor irritation to the reader, they cannot detract from the general high standard of a book which is clearly printed on good-quality paper and is well bound. At a price that is very reasonable by modern standards, it must inevitably find itself on the shelves of all interested in paper chromatography.

A. Robson

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952) and also, together with symbols and the periodicals abstracted, in the annual index*

I— PLANT; MACHINERY; BUILDINGS

PATENTS

Thread Storing and Advancing Reel. H. A. Kuljian. *USP* 2,645,918

A device for treating the thread with various liquids with means to prevent them mingling. C. O. C.

Wet Processing of Textiles in Continuous Lengths. William Franklin & Son. *BP* 711,475

The material passes through several small cells each containing a small volume of liquor. These cells are so shaped and arranged as to provide a long vertical or vertical U-shaped path for the material. The cells are constantly supplied with liquor in such a way as to set up zones of turbulence passing with wave-like motions through it. C. O. C.

Piece Dyeing Machine. F. Nestelberger. *BP* 710,833

The cloth is passed through a dyebath, squeezed and passed through a steam pressure chamber which it enters and leaves by liquid metal seals. C. O. C.

Conveying Material in Open Width or in Rope Form while maintaining Constant Tension. James Hunter Machine Co. *BP* 709,425

The radius of at least one of the transport rollers varies according to the pressure thereon of the material being conveyed. Each roller is driven at a predetermined angular speed. There is a device for retarding feeding of the material to the roll to a linear speed equal to the peripheral speed of the transport roll at a radius between its minimum and maximum radii. Thus the material is normally maintained under small tension as it passes between the retarding device and the transport roller, this normal tension sufficing to keep the radius of the transport roller such that its peripheral speed equals the rate of feed of the fabric. If the fabric stretches and so decreases the tension or shrinks and increases the tension the roll increases or decreases in radius and so in peripheral speed so as to keep the tension constant. C. O. C.

Heating Sheets or Webs. Grimsley & Co. (Leicester). *BP* 710,253

A machine occupying little space consists of a heat chamber which can be sealed, in which a wheeled carriage can be placed. This carriage carries an upper and a lower row of rods to support the web. C. O. C.

Tenter. H. Krantz Söhne. *BP* 709,972

The fabric passes through completely separated zones where it is treated in successive compartments alternately with hot air and superheated steam. This enables the temperature of the fabric to be controlled to suit the needs of any stage of drying without need to modify the temperature of the drying medium. Maximum drying effect per surface unit per hr. is attained without harmful effect. Expenditure of heat in air drying is restricted to that part of drying where its cost is justified by the better drying obtained. In addition, achievement of a high drying effect in the wet zone and a favourable finishing effect in the hygroscopic zone, and several other advantages are obtained. C. O. C.

Humidity Control in Drying Machines. Tomlinsons (Rochdale). *BP* 709,911

Some of the air in the drying chamber is continuously withdrawn through a small auxiliary chamber containing a cooling coil which cools the withdrawn air to $< 212°$F. without causing condensation. A wet and dry bulb thermometer lies in the path of cooled air and the reading is used to control the humidity in the drying chamber. C. O. C.

Covers for Preventing Escape or Entry of Dust into Finishing Machines. A. Monforts. *BP* 710,759

The body of the covers consists of moveable slats arranged as blinds. C. O. C.

Screen Printing Machine. Roto-Matic Screen Printer. *USP* 2,646,749

A machine in which the printing table can be adjusted to provide a printing surface of any vertical profile, even skew. C. O. C.

Silk Printing Screens. M. A. P. Forrester and R. J. Osborne. *BP* 711,269

A frame having devices to take up slack in the screen both longitudinally and laterally. C. O. C.

Liquid Coating of Paper and like Materials. Butterworth & Furnival. *BP* 711,806

Parallel endless chains are mounted on opposite sides of a frame. The chains are joined at intervals by bars bearing grippers to hold the paper. The chains are led over and under rollers or cylinders mounted across the frame. One of these rollers applies the liquid to the paper. Finally the paper passes through a heat drier. C. O. C.

Embossing Foil or other Material. Molins Machine Co. *BP* 711,471

Use of a thermoplastic material, especially Perspex, as the mating roller results in sharp impressions. Such rollers wear well and evenly, are not easily damaged and foreign matter does not tend to adhere to and clog them. C. O. C.

Setting, Drying or Similar Treatment of Hosiery. Dexdale Hosiery Mills. *USP* 2,646,194

The goods are placed on supports which move along a guideway into a chamber where steam or hot air is circulated. The chamber has doors at opposite ends and the guideway runs through it, one support being passed into the chamber concurrently with the removal of another, the doors being automatically opened and closed by the supports as they move along the guideway. C. O. C.

Ironing Machines. E. G. Opperman. *BP* 711,276

An electrically heated "iron" is moved towards an electrically driven roller for the ironing operation and away from the roller to a retracted position. C. O. C.

Garment Press. G. F. Grimsley. *BP* 711,772

Roller Hardener Machine for Felts. American Felt Co. *USP* 2,645,837

Detaching or Severing Natural Matter from Skins. Tanners' Research Corpn. *BP* 711,864

One or both sides of the skin is subjected to one or more fluid jets under sufficient pressure to remove adhering flesh or hair from the skin. C. O. C.

Electrostatic Coating Apparatus. Harper J. Ransburg Co. *BP* 710,852

Apparatus which ensures uniformity of distribution of the atomised coating material, and production of even coatings on both external, internal and recessed surfaces. C. O. C.

Printing with Flat Screens on a Cylindrical Base (IX p. 425).

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

PATENTS

Acid Esters of Orthophosphoric Acid and their Salts. ICI. *BP* 709,628

Very dilute aqueous solutions of *p-tert.*-octylphenyl dihydrogen phosphate and *p-tert.*-octylcresyl dihydrogen phosphates or their salts with alkali metals or monovalent non-metallic bases, are useful anti-slip agents for use in the spinning of artificial fibres. C. O. C.

Polyglycol Ethers of Phenols— Detergents, Dispersing and Levelling Agents. FBy. *BP* 710,982

Condensation of alkyl-substituted phenols (especially those with Alk of 6–12C) with the compounds obtained by reacting aldehydes (especially formaldehyde) with amides

of carboxylic acids (especially those of 2–7C), followed by treating the condensate with alkylene oxides, yields polyglycol ethers of phenols which either as such or after sulphonation are useful as detergents over a wide range of pH and as dispersing and levelling agents. C. O. C.

Size. DuP. *USP* 2,646,412

An aqueous solution of polymethacrylic acid and urea while being readily removed from textiles if allowed to remain in the finished product improves its appearance and wearing qualities. Nylon sized with this solution can be heat set without any deleterious effect or the size being rendered immovable. C. O. C.

Anti-static Agents. Johnson & Johnson (Gt. Britain). *BP* 709,555

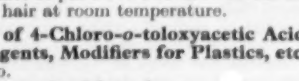
The long chain fatty acid partial esters of (*a*) aliphatic polyhydric alcohols (*b*) the anhydrides of such alcohols, or (*c*) polymers of aliphatic polyhydric alcohols, the polymers containing 2–6 C and 2–6 OH, and the polyoxyalkylene ethers of such esters are excellent anti-static agents for application to many non-cellulosic man-made fibres. Thus Saran upholstery fabric is rendered astatic by treatment with a 0·125–5·0% solution of sorbitan monolaurate in an oil-free hydrocarbon solvent or an aqueous suspension of that strength. The solution or dispersion can be applied in any manner and after drying imparts an astatic finish fast to rubbing and repeated washing with aqueous soap solution. C. O. C.

Swelling Agent for Use with Alkali Metal Bisulphites in the Cold Waving of Hair. Warner-Hudnut. *BP* 711,060

Agents of formula $X{\cdot}CO{\cdot}NR^1R^2$ (X = H, CH_3 or NH_2; R^1 and R^2 = same or different, H, alkalonol or Alk of < 5C), e.g. urea or formamide, are used with an alkali metal bisulphite at pH 6·5–7·5 so as to obtain maximum swelling of the hair at room temperature. C. O. C.

Ester of 4-Chloro-*o*-toloxyacetic Acid—Rotproofing Agents, Modifiers for Plastics, etc. Dow Chemical Co. *BP* 711,680

Compounds of formula—



($n < 4$; R = Alk or phenyl) are used as modifiers for plastics and as preservatives for paper, wood and cellulosic materials. They are oily liquids, somewhat soluble in many organic solvents and insoluble in water. C. O. C.

Diazotype production of Photomechanical Printing Plates (IX p. 425).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Enzymatic Reduction of Aromatic Nitro, Nitroso, and Hydroxylamino Compounds. I. Yamashina, S. Shikata, and F. Egami. *Bull. Chem. Soc. Japan*, **27**, 42–45 (Feb. 1954).

An enzyme preparation of a halotolerant bacterium activates aromatic nitroso and hydroxylamino compounds as well as nitro compounds and accelerates their reduction by hydrogen donor systems. The reduction of nitroso and hydroxylamino is more strongly inhibited by cyanide and azide than that of nitro. Azoxy, azo, and hydrazo compounds are not reduced by the enzyme system. Special enzymes, such as nitrosoreductase, hydroxylaminoreductase, and nitroreductase, are suggested. Reaction velocity and paper chromatography studies of intermediates and end products suggest the following scheme for enzymatic reduction of nitro to amino—

Nitro → Nitroso → Amino
↘ Hydroxylamino

W. R. M.

Enzymatic Reduction of Aromatic Nitro Compounds. I. Yamashina. *Bull. Chem. Soc. Japan*, **27**, 85–89 (March 1954).

An enzyme, "nitroreductase", which activates aromatic nitro compounds and accelerates their reduction, was extracted from a halotolerant bacterium. Reduction involves nitroreductase, an intermediary hydrogen carrier, dehydrogenase, and a hydrogen donor. Oxazine dyes are the only effective hydrogen carriers so far examined. Various aromatic nitro compounds can be reduced to amino compounds by the enzyme system. The nitroreductase is not considered to be identical with nitrite reductase.

W. R. M.

Aromatic Azo Compounds. V—Absorption Spectra of *N*-Substituted 4-Aminoazobenzenes and their Mono-acid Salts. G. M. Badger, R. G. Buttery, and G. E. Lewis. *J.C.S.*, 1888–1890 (June 1954).

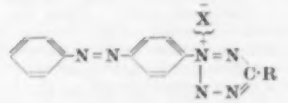
The absorption spectra of 4-aminoazobenzenes and of some *N*-substituted deriv. in neutral and in acid soln., afford, in general, two absorption bands for the mono-acid salts in the region 5000–5400A, and at 3200A. The results support the view that the salt cations exist in solution as an equilibrium mixture of two tautomeric forms, in which the protein is attached to the azo linkage and to the amino group respectively; their ionisation constants are determined from the spectra. H. H. H.

Oxidation of Phenylhydrazones—III. B. M. Lynch and K. H. Pausacker. *J.C.S.*, 1650 (May 1954).

Witkop and Kissman's (*J. Amer. Chem. Soc.*, **75**, 1975 (1953)) benzaldehyde phenylhydrazone, obtained by $LiAlH_4$ reduction of the peracid oxidation product of benzaldehyde phenylhydrazone (viz. benzylazoxybenzene), is now found to be a stereoisomer of it (probably the *cis* form), since a mixed m.p. with the *trans* (normal) compound is 20°c. depressed. Similar reductions of *p*-methoxybenzylazoxybenzene, *p*-benzylazoxychlorobenzene, and *p*-benzylazoxytoluene give the "normal" substituted benzaldehyde phenylhydrazones. H. H. H.

Tetrazolium Compounds. II—Azo Derivatives. D. D. Libman, A. W. Nineham, and R. Slack. *J.C.S.*, 1565–1568 (May 1954).

The preparation of substituted deriv. of I is described, where in each compound an *N*-phenyl group bears a phenylazo substituent. Effects of substitution in the benzene rings have been examined, and two bistetrazolium salts have been obtained (polymethylene bridge at R).

(I) 

H. H. H.

Electrophilic Reactivity of Alkoxyalkylidene Derivatives of Heterocyclic Keto-methylene Compounds. E. B. Knott. *J.C.S.*, 1482–1490 (May 1954).

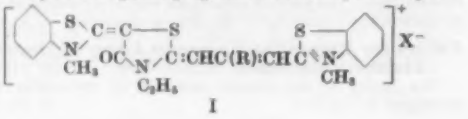
Certain cyclic keto-methylene compounds condense with orthoesters to give 1-alkoxyalkylidene deriv., certain of which are converted into dimethin*mero*cyanines substituted by alkyl in the chain. 5-1′-Alkoxyalkylidenerhodanines react with NH_3 or primary or secondary amines to give 5-1′-aminoalkylidenerhodanines, which are quaternised by methyl toluene-*p*-sulphonate and thence condensed with heterocyclic keto-methylene compounds to give complex *mero*cyanines. Electronic explanations are given of these reactions. H. H. H.

Nucleophilic Reactivity of Alkylidene Derivatives of Cyclic Keto-methylene Compounds. E. B. Knott. *J.C.S.*, 1490–1501 (May 1954).

3-Substituted rhodanines condense with acetaldehyde, crotonaldehyde, acetone, diacetyl, and pyruvic acid to give 4-alkylidene deriv. These and the 1′-alkoxy- and 1′-alkylthio-ethylidene deriv. of a number of cyclic keto-methylene compounds have been condensed with electrophilic cyclic quaternary ammonium salts to give simple and complex *mero*cyanines and oxamines. Some of these complex dyes have their main absorption band almost completely in the infrared region, a phenomenon which appears to be unique for non-ionic dyes. H. H. H.

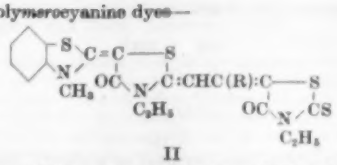
Photographic Sensitisers of the Trinuclear Series. IV. A. E. van Dormael. *Industrie chim. belge.*, **18**, 1297–1302 (1953): *Chem. Abs.*, **48**, 6297 (10 June 1954).

A study of the optical properties of rhodacyanine dyes—



I

and of polymerocyanine dyes—



II

Replacement of R = H or CH_3 by R = OCH_3 in I produces a hypsochromic effect of the same order of magnitude as in the corresponding sym. trimethin cyanines. Comparison of the optical data of II with similarly substituted dimethinmerocyanines shows a slight hypsochromic effect when the ethoxy group is substituted for H or CH_3 as R.
C. O. C.

Yellow Sulphur Dyes by Fusion of Sulphur, Benzidine and Toluene-2:4-diamine. H. Hiyama and T. Urahata. *J. Chem. Soc. Japan*, Ind. Chem. Sect., **55**, 670–1 (1952): *Chem. Abs.*, **48**, 6699 (10 June 1954).

The yellow sulphur dyes obtained by fusing 1 mol. of benzidine with 1 or 2 mol. of toluene-2:4-diamine and S at 200°c. have the empirical formulæ $C_{19}H_{14}N_4S_2$ and $C_{26}H_{18}N_4S_4$ respectively. Their chemical structure is discussed.
C. O. C.

Dyes for Acetate Rayon. I— Dyeing Properties and Preparation of (2-Hydroxyethylamino) anthraquinones. Y. Bansho. *J. Chem. Soc. Japan*, Ind. Chem. Sect., **55**, 666–9 (1952): *Chem. Abs.*, **48**, 6701 (10 June 1954).

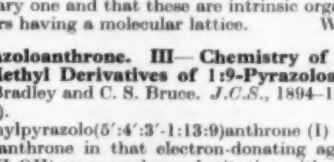
Of 21 derivatives examined, the 1-, 1-amino-4-, 1:4 bis- and 1-methylamino-4-, (2-hydroxyethylamino) anthraquinone, 1:4-bis(2-hydroxyethylamino)-5:8-dihydroxy anthraquinone and 1-(2-hydroxyethylamino)-4-(*p*-aminoaniline)anthraquinone seemed to have potential use as disperse dyes.
C. O. C.

Photoconductivity of the Condensed Polynuclear Aromatic Compounds. H. Inokuchi. *Bull. Chem. Soc. Japan*, **27**, 22–27 (Feb. 1954).

Photoconductivity and optical absorption in the solid state of *iso*violanthrone, violanthrone, *iso*violanthrene, violanthrene, pyranthrone, pyranthrene, ovalene, flavanthrone, indanthrone, and indanthrazine have been measured. The energy gap between the full and the empty bands has been estimated. Results are in agreement with values estimated from the temperature dependence of electrical resistivity. It is suggested that the photocurrent is a primary one and that these are intrinsic organic semiconductors having a molecular lattice.
W. R. M.

1:9-Pyrazoloanthrone. III— Chemistry of the Two *N*-Methyl Derivatives of 1:9-Pyrazoloanthrone. W. Bradley and C. S. Bruce. *J.C.S.*, 1894–1902 (June 1954).

1′-Methylpyrazolo(5′:4′:3′-1:13:9)anthrone (I) resembles *meso*benzanthrone in that electron-donating agents (e.g. KOH–C_2H_5OH) cause nuclear substitution with or without self-union of I. With the same reagents 1′-methylpyrazolo (3′:4′:5′-1:13:9)anthrone (II) undergoes self-union almost exclusively. The enhanced ease of self-union of II is related to its *o*-quinonoid form.



(I)

(II)

H. H. H.

Sulfogene Brilliant Green J and Sulfogene Brilliant Blue BGL. H. Hiyama, T. Urahata, and Y. Nakamura. *J. Chem. Soc. Japan*, Ind. Chem. Sect., **55**, 669–670 (1952): *Chem. Abs.*, **48**, 6699 (10 June 1954).

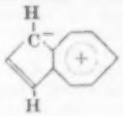
Assuming that Sulfogene Brilliant Green J is a trisulphide of copper phthalocyanine, mainly trimercaptan, a similar dye was produced from copper phthalocyanine. Similarly it is shown that Sulfogene Brilliant Blue BGL is a sulphurous compound of dimethylanilineindophenol.
C. O. C.

Synthesis of Fluorescent Organic Compounds. XIII Emissivity of Fluorescence of Napth-1:2-iminazoles and Perimidines. Fluorescence of the Synthetic Compounds. Z. Yoshida and R. Oda. *J. Chem. Soc. Japan*, Ind. Chem. Sect., **55**, 565–6 (1952): *Chem. Abs.*, **48**, 6261 (10 June 1954).

Comparison of six naphth-1:2-iminazole derivatives with six perimidine derivatives showed the former group to be the more strongly fluorescent.
C. O. C.

Fine Structure of Azulene. W. H. Stafford and D. H. Reid. *Chem. and Ind.*, 277–278 (6 March 1954).

Independent evidence, based on the similarities between azulenes and the anhydro-salts, is advanced to support the assignment of betaine-type structures to the reacting forms of azulene (c.f Anderson, Nelson, and Tazuma, *J. Amer. Chem. Soc.*, **75**, 4980 (1953)). The structure I, in which the cationic function is fulfilled by the *cyclo*heptatrienyl ion, is suggested.



(I)

A. J.

Chemistry of the Melanins. V— Autoxidation of 5:6-Dihydroxyindoles. R. J. S. Beer, T. Broadhurst, and A. Robertson. *J.C.S.*, 1947–1953 (June 1954).

The autoxidation of 5:6-dihydroxyindoles, whereby melanin-like pigments and H_2O_2 are formed, is now examined by measurements of oxygen uptake, by elementary analysis of the pigments produced, and by spectroscopic studies of intermediates obtained by enzymic and Ag_2O oxidation. With Ag_2O, yellow indole:5-6-quinones of varying degrees of stability are obtained. The results, while supporting the quinone polymerisation theory of melanin formation, indicate that some of the component indole units are more extensively oxidised.
H. H. H.

Chemistry of Extractives from Hardwoods. XVI— Coumarin Constituents of *Fagara macrophylla*, *Zanthoxylum flavum* and *Chloroxylon swietenia*. F. E. King, J. R. Housley, and T. J. King. *J.C.S.*, 1392–1399 (May 1954).

The two former title substances are from West Indian satinwoods and their cryst. heartwood extractives are mainly 6:7-dimethoxy- and 6:7:8-trimethoxy-coumarin, suberosin (7-methoxy-6-*iso*pent-2′-enylcoumarin), and peoralene (furano (2′:3′-6:7) coumarin), whereas the last named is from East Indian satinwood and its extractives are chiefly xanthyletin (2′:2′-dimethylpyrano (5′:6′-6:7) coumarin), xanthoxyletin (5-methoxyxanthyletin), and the related but previously unknown phenol, 7-demethylsuberosin.
H. H. H.

Chemistry of Extractives from Hardwoods. XVII— Occurrence of a Flavan-3:4-diol (Melacacidin) in *Acacia melanoxylon*. F. E. King and W. Bottomley. *J.C.S.*, 1399–1403 (May 1954).

The amorphous material extracted by ether from Australian Blackwood (*Acacia melanoxylon*) is mainly melacacidin (3:4:7:8:3′:4′-hexahydroxyflavan), which combines the properties of both *leuco*anthocyanidin and phlobatannin, thereby indicating a flavan-3:4-diol structure for this widely distributed group of natural products.
H. H. H.

A New Pigment, Digitolutein, from the Leaves of *Digitalis purpurea*. R. A. Paris. *Compt. rend.*, **238**, 932–4 (1954): *Chem. Abs.*, **48**, 6408 (10 June 1954).

A yellow pigment, $C_{19}H_{16}O_8$ containing one methoxy group which does not give the typical colour reactions of flavonoids and is probably a naphthoquinone.
C. O. C.

Stepwise Dehydrogenation of the Colourless Polyenes Phytoene and Phytofluene with *N*-Bromosuccinimide to Carotenoid Pigments. L. Zechmeister and B. K. Koe. *J. Amer. Chem. Soc.*, **76**, 2923–6 (5 June 1954).

Dehydrogenation of the colourless plant polyenes phytoene and phytofluene can be carried out with *N*-bromosuccinimide and some other compounds. The process is stepwise and takes place mainly at the ends of the

conjugated system and leads through the following series—phytoene → phytofluene → ζ-carotene → neurosporene → lycopene. The exact mechanism of some of the steps is unknown. C. O. C.

Dyes of Ancient Peru. G. A. Fester and J. A. Retamar. *Rev. fac. ing. quím.* (Santa Fé, Argentine), **21–22**, 133–143 (1952–53): *Chem. Abs.*, **48**, 6701 (10 June 1954).

Indigofera suffruticoa was used to dye blues to bluish blacks. Al salts of laccaic acid were used to make carmine. The source of yellow dyes was not traced but the fibres did not contain iron. Some reds were obtained by applying tannins on a ferric sulphate mordant. C. O. C.

Red Dyes used by South American Indians. G. A. Fester. *Rev. fac. ing. quím.* (Santa Fé, Argentine), **20**, 105–116 (1951): *Chem. Abs.*, **48**, 6700 (10 June 1954).

Red dyes used in the earlier Paracas period were from some of the 25 species of *Relbunium*; they vary in the content of derivatives of purpurin, pseudopurpurin, xanthopurpurin and alizarin which makes them adaptable to producing any desired variety of red when used with alumina, aluminium sulphate, ash of "urao" which contains Na_2CO_3, "culle" (*Oxalis rosea*) which contains potassium oxalate and ferric hydroxide, and when used at different pH. A vivid carmine was produced in this way. Carminic and quermesic acids were found only in the remains of textiles from later civilisations; the acids could have been introduced by the *Dactoylopius* culture from Mexico or Guatemala. An orange dye, lanigerin, a quinizarin derivative from *Eriosoma lanigerum*, a yellow dye from *Pedronia festeriana* and a brownish red from *Icerya purchasi* were found during the investigation of probable dye sources. C. O. C.

Production of Dyes and Pigments in Spain. G. Inskeep. *Chem. Eng. News*, **32**, 2496 (21 June 1954).

About 70% of Spanish dye production is by Fabricación Nacional de Colorantes y Explosivos, smaller makers being Anilinas, Colorificio, Materias Colorantes and Cardoner y Cia. Annual production of azo dyes is approx. 1000 tons. Lithopone is Spain's most important pigment, the annual production of 10,000 tons being consumed internally with no raw materials needing to be imported; the two largest producers are S. A. Nevin and Unión Química del Norte de España. There is capacity for producing 10,000 tons of zinc oxide per annum but full capacity has not been reached because of lack of raw materials. Producing capacity for titanium dioxide is 3000 tons per annum and as Spain's own requirements are only 500 tons per annum, large amounts are available for export. Spanish annual requirements of red and white lead are about 4500 tons but scarcity of the metal has restricted domestic production. Several plants are producing lead pigments, two by electrolytic processes. C. O. C.

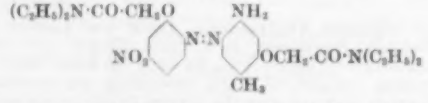
Textiles and Dyes at the Frankfort Fairs. F. Lerner. *Ciba Review*, **9**, 3696–3718 (April 1954).

Historical, covering the last six centuries. C. O. C.

PATENTS

Stabilised Diazonium Salts. FH. *BP* 711,617

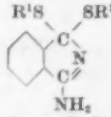
o-Aminomonoazo compounds containing one or more $-OCH_2{\cdot}CO{\cdot}NAlk_2$ groups as substituents in an aryl nucleus are more readily diazotisable than similar compounds not containing this group, and yield more soluble diazo compounds and $ZnCl_2$-diazonium chloride double salts. Thus the compound—



gives a $ZnCl_2$-diazonium chloride double salt whose solubility in water is equivalent to 17·1 g. of base per litre, whereas the similar double salt containing two OCH_3 groups instead of the $-OCH_2{\cdot}CO{\cdot}N(C_2H_5)_2$ groups has a solubility equivalent to 9·8 g. of base per litre. E. S.

3-Amino-*iso*indolenine Derivatives—Phthalocyanine Formers. ICI. *BP* 711,433

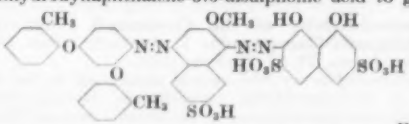
Phthalonitrile is treated with an alkyl-, hydroxyalkyl- or aralkyl-mercaptan in presence of an alkoxide, or hydroxide of an alkali or alkaline earth metal, or a strong organic base to give 3-amino-*iso*indolenine derivatives of formula—



(R^1 and R^2 = Alk, hydroxyalkyl or aralkyl.) Thus ethyl mercaptan followed by powdered phthalonitrile is added to a soln. of sodium in methanol at 0–2°C. After 72 hr. at this temperature the resulting white solid is filtered off, added to 5% aq. $NaHCO_3$ and air passed to remove excess mercaptan. The products when padded on to cotton for example in presence of ethanol, glycol and sodium acetate, and with or without a metal compound such as the Cu complex of disodium ethylenediaminetetra-acetate, followed by baking at 130–150°C. produce fast blue-greens. R. K. F.

Disazo Blue-green Dyes for Colour Photography. Gy. *BP* 711,232

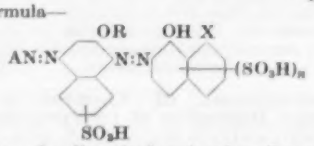
Disazo compounds made by diazotising aminophenylbenzyl ethers or aminodiphenyl ethers (which may contain substituents, e.g. ether groups, but not water-solubilising acid groups), coupling with 2-alkoxy (or carboxymethoxy)-1-naphthylamine-6(or 7)-sulphonic acids, rediazotising and coupling with a 1:8-dihydroxy- or 1-amino-8-hydroxy-naphthalenemono(or di)sulphonic acid, dye gelatine pure blue–green, and show little or no tendency to diffuse into adjacent gelatine layers of colour photography films. In the silver-dye-bleach process they require only a short bleaching time. Thus diazotised 2:4-bis-*o*-methylphenoxyaniline is coupled under weakly acid conditions with 2-methoxy-1-naphthylamine-6-sulphonic acid, and the aminomonoazo compound so formed is rediazotised and coupled in the presence of ammoniacal pyridine with 1:8-dihydroxynaphthalene-3:6-disulphonic acid to give—



E. S.

Cyan Dyes for Use in Colour Photography. Gy. *BP* 711,233

Dyes of formula—



(A = residue of a diazotised aminophenylbenzyl ether or of a diazotised aminophenyl-phenyl ether which may contain in the benzene ring additional substituents usually found in azo dyes, particularly additional ether groups but no water-solubilising groups; R = Alk or carboxymethyl; X = OH, NH_2, alkylamino, aralkylamino, acylamino or sulphonamido; n = 1 or 2) are used as bleachable dyes in silver halide emulsion layers. C. O. C.

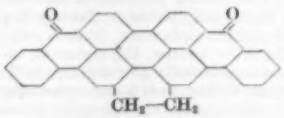
Acridone Vat Dye Leuco-Sulphuric Esters. American Cyanamid. *BP* 710,301

The leuco-sulphuric esters of phthaloyl-acridone vat dyes are made by treating the corresponding 1-arylamino-2-carboxyanthraquinones with Zn, Fe or Cd and the addition compound of SO_3 and a tertiary amine of dissociation constant $< 1 \times 10^{-7}$. Cyclisation takes place at the same time as esterification. Thus chlorosulphonic acid is added to a mixture of trimethylamine and chlorobenzene at 5–10°C. 1-(β-Naphthylamino)-2-carboxyanthraquinone is added to the resulting slurry under N_2 at room temperature, followed by Zn at 50°C. Separation is effected by pouring into aq. Na_2CO_3/NaOH and removing the chlorobenzene and trimethylamine by distilling under reduced pressure. *BP* 710,302

The same products are obtained by carrying out the reduction, esterification and cyclisation in aq. alkaline solution, using $Na_2S_2O_4$ as reducing agent and an addition compound of SO_3 and a tertiary base as already described. R. K. F.

Dibenzanthrone Derivatives containing an Ethylene Bridge—Vat Dyes. Eastman Kodak. *USP* 2,637,733

10-Methyleneanthrone and its halogenated derivatives are condensed with 1:3-cyclohexadiene in presence of an oxidising agent. The dibenzanthronyls so obtained are converted to the corresponding dibenzanthrone in alcoholic KOH. Thus 10-methyleneanthrone is refluxed for 6 hr. with 1:3-*cyclo*hexadiene in a mixture of acetic acid and acetic anhydride. The product is heated at 130–145°C. with ethanol and KOH. After diluting with water and passing air through the resulting solution there is obtained the blue vat dye—



which may be further oxidised in alcoholic KOH with e.g. $NaNO_3$ to produce a bordeaux vat dye. R. K. F.

Chloromethylated Benzanthronylpyrazoloanthrones. General Aniline. *USP* 2,619,487

The change of colour when dyeings of Indanthren Navy Blue R are spotted with water is eliminated by introducing 1 or 2 chloromethyl groups by treating the dye with dichlorodimethyl ether in H_2SO_4. This is done at 25–60°C., the resulting products dyeing greener blues than the original dye. R. K. F.

Metal Phthalocyanines. General Aniline. *BP* 711,376

The yield and purity of metal phthalocyanines obtained in processes of the phthalic anhydride–urea–metal salt–organic solvent type are improved by having present during the reaction 25% to 100% by weight of the phthalic anhydride or related compound, of H_2SO_4, sulphamic acid, an alkyl sulphate, alkali metal sulphate or alkaline earth sulphate. Thus, all parts being by weight, a slurry of $AlCl_3$(3) in trichlorobenzene (5) is added to a mixture of phthalic anhydride (10·5), urea (12·5), ammonium molybdate (0·25), Na_2SO_4 (5·4) and trichlorobenzene (35) at 200–205°C. over 6 hr. Urea (5·4) in trichlorobenzene (10) is then added and the whole heated for 5 hr. at the same temperature. Chloroaluminium phthalocyanine is obtained in 85% yield. R. K. F.

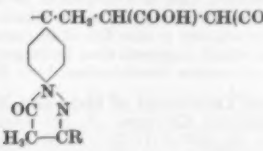
Polymethin Quinoline Dyes. Eastman Kodak Co. *USP* 2,646,430

Production of polymethin dyes containing the group—

(Z = atoms to complete a pyrrole, pyridine or thiazine) and of 11 different general formulæ is described. C. O. C.

Polymeric Pyrazolone Colour Couplers. Eastman Kodak Co. *USP* 2,646,421

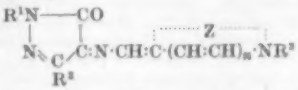
The copolymer of styrene and maleic hydride is nitrated and then reduced by the method of *USP* 2,274,551. The polyamine so obtained is diazotised and reduced to the hydrazine. This is then reacted with a compound which will result in a polymer having the recurring formula—



(R = CH_3, carboxy, phenyl, *p*-methoxyphenyl, amino or benzamido). The product is a pyrazolone coupler combined with a polymeric grouping so as to anchor the complex and any dye formed from it. C. O. C.

Aza*mero*carbocyanine Dyes. Eastman Kodak Co. *USP* 2,646,409

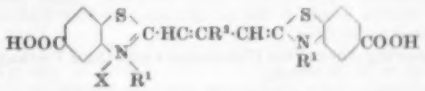
Dyes of formula—



(R^1 and R^3 = Ar, Alk and R^1 may = benzothiazolyl; n = 0 or 1; R^3 = Alk or Ar; Z = atoms to complete a thiazole, naphthothiazole, thionaphthene-7′:6′:4:5-thiazole, naphthoxazole, selenazole, benzselenazole, naphthoselenazole, thiazoline, 2-quinoline, 4-quinoline, 1-*iso*quinoline, 3-*iso*quinoline or pyridine nucleus) while having no sensitising effect on silver halide emulsions are excellent supersensitisers for certain cyanine dyes many of which themselves have no sensitising effect. C. O. C.

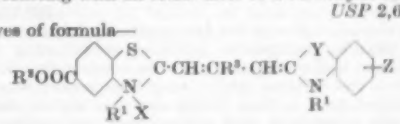
5-Carboxybenzthiazolecarbocyanine Dyes. DuP. *USP* 2,647,050

Dyes of formula—



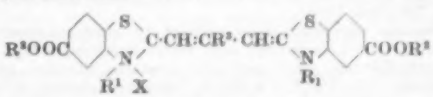
(R^1 = Alk of 1–2C or benzyl; R^2 = H or hydrocarbon; X = anion) are made from 2-methyl-5-carboxybenzthiazole by converting it into a *cyclo*ammonium salt and then reacting with an ortho ester of a carboxylic acid. *USP* 2,647,051

Dyes of formula—



(R^1 = Alk; R^2 = Alk of 1–4C; R^3 = H or Alk of 1–3C; X = anion; Y = S or Se; Z = H, Alk of 1–3C, Ar of 4–10C Cl, Br or alkoxy of 1–3C) are made by condensing a 2-(*β*-anilino) (or *β*-acetanilino)-vinyl-5-carboxymethoxy benzthiazole quaternary salt with a 2-methylbenzothiazole or a 2-methylbenzoselenazole quaternary salt in presence of an acid binding agent and then heating under reflux conditions. *USP* 2,647,052

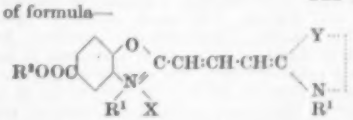
Dyes of formula—



(R^1 = Alk of 1–3C or benzyl; R^2 = Alk of 1–4C; R^3 = H or Alk of 1–3C; X = anion) are made from a 2-methylbenzthiazole containing a carbalkoxy substituent of 2–5C in the 5-position of the benzothiazole ring by converting it into a *cyclo*ammonium or quaternary salt and condensing this with an ortho ester of a monocarboxylic acid. *USP* 2,647,053

Dyes of the above formula in which S is replaced by O and R^2 = H or Alk, are similarly made. *USP* 2,647,054

Dyes of formula—



(R^1 = Alk; R^2 = Alk of 1–4C; X = anion; Y = atoms to complete a thiazoline, benzothiazole, naphthoxazole, subst. benzoxazole free from ester substituent, benzoselenazole, naphthothiazole, naphthoselenazole and dimethylindolenine radical) are made by condensing a 2-(*β*-anilino) (or *β*-acetanilino-vinyl-5-carbalkoxybenzoxazole quaternary salt with a quaternary salt of a thiazoline, benzoxazole, benzothiazole, benzoselenazole, naphthiazole, naphthoxazole or naphthoselenazole which contains a reactive CH_2 group in *α*-position to the heterocyclic N atom. C. O. C.

Deleafed Aluminium Pigments. Aluminium Laboratories. *BP* 711,345

A mixture of a surface acting silicone compound, a fatty acid of formula $C_nH_{2n+1}COOH$ (n = 3–9) and an aliphatic or alicyclic amine dispersed in mineral spirits is mixed with the pigment to produce non-leafing paste-type aluminium pigments. They may be dried to powder and are brighter than the non-leafing pigments hitherto known. C. O. C.

Titanium Pigment. National Titanium Pigments. *BP* 711,833

Titanium ore or concentrate mixed with an alkali metal compound is oxidised at 500–1000°C. using 2 atoms alkali metal for every 5 atoms Ti together with enough excess of the alkali metal compound to convert into water-soluble alkali metal oxidation products all the elements present which can be so converted. Finally the mixture is extracted with water. The product is an intermediate for making TiO_2 by processes using H_2SO_4 and may in some cases be directly used as a pigment. C. O. C.

Cleansing Witherite. National Coal Board. *BP* 711,631

Increased yield and/or faster flotation, easier filtering and dyeing result if the conditioning and/or frothing is affected at 25–55°C. C. O. C.

Colouring Agents for Elastomers and their Packaging. R. B. F. F. Clarke. *BP* 711,214

A mixture of a pigment, a rubber antioxidant of resin type, e.g. Nonox EX, a detackifier, e.g. paraffin wax, and an extender, e.g. mineral oil, is non-dusting, clean to handle and readily incorporated into elastomers by normal techniques used in the rubber and plastics industries. *BP* 711,215

The above mixture is fed into a tube of polyethylene or other flexible transparent material of softening point higher than that of the mixture. The whole is then heated to soften the mixture while being compressed laterally. The loaded tube is then folded down in zig-zag fashion while the mixture is still soft so that, on setting, the compressed mixture is disposed in a compact arrangement of individually enclosed flakes. C. O. C.

Electrophoresis of Pigments in Organic Solvents— IV (V below).

V— PAINTS; ENAMELS; INKS

Electrophoresis of Pigments in Organic Solvents. IV. H. Brintzinger, R. Haug and G. Sachs. *Farbe u. Lack*, **60**, 15–24, 59–68, 95–103 (1954): *Chem. Abs.*, **48**, 6710 (10 June 1954).

Organic pigments were subject to electrophoresis in methyl, ethyl, *iso*propyl and butyl alcohols, $(CH_2OH)_2$, dimethylketone, ethyl and butyl acetates, dioxane, nitrobenzene, CCl_4, CH_2Cl_2, $C_2H_3Cl_3$, benzene, toluene, xylene, tetra- and decahydronaphthalenes, dipentene and mineral spirits. In nonpolar solvents almost all organic pigments were precipitated at the electrodes; only Heliogen Blue and certain lake colours (Orange II, Orange II RN) showed "dancing" and "bridge formation", i.e. flocculation. The charge assumed by the pigments was affected by substituents, e.g. sulpho groups tended to produce a positively charged pigment except in presence of Cl or NO_2 groups, by wetting agents and by excess precipitant ions. Thus aqueous extraction of some pigments followed by drying at 110°C. reversed their charges. Commercial pigments, both inorganic and organic, hold much moisture. Tests were made by the Seaman, Comas and Allen method. Pigments which still retained $> 0{\cdot}1\%$ water flocculate in non-polar and weakly polar solvents, but anhydrous pigments, e.g., Chrome Green dried at 200°C. over P_2O_5 under 15 mm. Hg, precipitate at the anode without flocculation and show reduced sedimentation volume. Current intensities of pigment slurries in CCl_4 (in fields from 100v.–10kv./cm.) rose sharply with bridge formation or dancing and with pigment concentration, and linear relations existed in log-log presentation. The increased conductivity is caused by films of moisture, electrolyte content (e.g. in TiO_2), decreased particle size (e.g. with microdolomite and Milori Blues), and the intrinsic conductivity of the pigment. Pigments capable of high moisture absorption show high tendency to flocculate in non-polar solvents. Moisture, not adsorbed air, caused flocculation and large sedimentation volume. Addition of 0·1% of methyl, ethyl, or butyl alcohol, methyl acetate or $(CH_2OH)_2$ caused Chrome Green in CCl_4 to flocculate, but a 20% addition merely produced whirling without precipitation at the electrodes. Other less-polar solvents had not this effect. The least sedimentation volumes were usually found in those solvents where there was no flocculation. Pigments of opposite charge precipitated one another even in polar solvents, though not in all ratios. Flocculating pigments bring down non-flocculating pigments with them; large excess of one pigment reversed the charge of another, normally oppositely charged, pigment mixed with it. A mixture of TiO_2 and Heliogen Blue held the charge of the latter until the ratio exceeded 9:1. Mixtures of oppositely charged pigments settle out much more quickly than either pigment alone. Wetting agents (particularly Nekal BX, Nekal A, Turkey Red oil, Basopal NA, dodecylbenzenesulphonate, hydroxyalkylamine salts of fatty acids, ACO wetter, Emulphor A oil-soluble, and lecithin) added to slurries of Chrome Green, TiO_2, Heliogen Blue and Hansa Yellow in toluene or tetrahydronaphthalene, slowed sedimentation considerably in most cases. The Nekals and Basopal NA imparted positive changes to all the pigments, while all the other wetting agents had only a deflocculating effect, i.e. they increased the zeta potential. Turkey Red oil increased the flocculation of the two organic pigments. Chlorinated rubber (Pergut S40) and cyclised rubber (Alpex 450J) showed high deflocculating and dispersing properties. 131 references. C. O. C.

PATENT

Dull Lacquers. G. B. Heijmer. *BP* 711,545

Condensation of urea- and/or melamine-formaldehyde resins, cellulose nitrate and alkyd resins in a solvent yields an excellent dulling medium which when used in lacquers affects neither the transparency nor the smoothness of the film and which does not tend to settle out. C. O. C.

VI— FIBRES; YARNS; FABRICS

Deformation of Regenerated Cellulose Fibres. III— Deformation and Refractive Indices of Air-dried Filament. S. Okajima and S. Hayama. *Bull Chem. Soc. Japan*, **27**, 61–64 (Feb. 1954).

Ramie, hydrolysed to give three samples of differing degrees of polymerisation, was dissolved in cuprammonium soln. and spun to give model filaments. Results of stretching and refractive index determinations suggest that deformation of dried filaments can be expressed in terms of Kratky's first theory. This behaviour is unaffected by changes in the temperature of spinning or in concentration of cellulose solution. Less humid drying conditions result in orientation effects in the early stages of stretching. W. R. M.

Microbiology of Cellulosic Textiles. H. Ostertag. *Melliand Textilber.*, **35**, 224–226 (March), 340–344 (April), 486–488 (May 1954).

The relevant types of micro-organisms are reviewed, the important ones being described in greater detail and illustrated by photomicrographs. Methods of protection against microbes are discussed. H. E. N.

Hindered Dissociation of the Phenol Group of Fibroin. E. Schauenstein, O. Kratky, and O. Gold. *Melliand Textilber.*, **35**, 375–378 (April 1954).

Phenolic dissociation curves are determined spectrophotometrically for tyrosine, glycyltyrosine, and three forms of fibroin (denatured soln.; denatured, rolled and stretched film; and natural, rolled and stretched film). The dissociation is shown to decrease in the order given, particularly on converting the semiglobular dissolved form of fibroin into the fibrillar solid condition. Taking X-ray data into consideration, this is interpreted as a reaction limited to the surface of micelles in weak alkali. In later work, hindered dissociation is also found in monodisperse dissolved proteins, which suggests that hydrogen-bonding is its cause, here and within the micelles. H. E. N.

Thioglycollic Acid Treatment of Hair and Reformation of Disulphide Groups. A. Schöberl. *Naturwissenschaften*, **40**, 390–1 (1953): *Chem. Abs.*, **48**, 6653 (10 June 1954).

When hair is cold waved by thioglycollic acid and H_2O_2 the total S content increases from 5·28 to 6·49% for human hair, 3·45 to 4·03% for wool and 4·00 to 4·42% for horse hair; the cystine content does not increase to the same

degree. It is assumed that this is due not only to reformation of S:S bonds but particularly to a tying up of SH groups from cysteine residues to SH groups of thioglycollic acid under the influence of H_2O_2. Hence the hydrolysate of the treated hair should contain the asymmetric disulphide $COOHCH(NH_2)CH_2SSCH_2COOH$. This seems likely from presence of alkali-labile S:S groups as shown by the plumbite test. C. O. C.

PATENTS

Pigmentation of Viscose. Kuhlmann. *BP* 711,977

The pigment is dispersed in a solution of an alkali-soluble water-insoluble polyhydric alcohol cellulose ether, e.g. glycol cellulose or propylene glycol cellulose, and then added to the viscose immediately before it is extruded. C. O. C.

Loosening Rayon Cakes by Simultaneous Soaking and Deformation. American Viscose Corpn. *USP* 2,646,342

The cake is fed between two surfaces arranged one above another in converging direction and travelling at different speeds and in opposite directions or in the same direction. The longitudinal axis of the cake extends transversely to the surfaces. The cake is rolled along in the direction of the surfaces while partly submerged in an inert liquid. C. O. C.

Polyacrylonitrile Fibres, Films, etc. BrC. *BP* 711,344

A solution of polyacrylonitrile is extruded or cast into a coagulant liquid containing as its sole or chief constituent a liquid aromatic hydrocarbon or a liquid halogenated aliphatic hydrocarbon. C. O. C.

Elastic Linear Copolyester Fibres, Films, etc. DuP. *BP* 711,279

A product suitable for producing fibres, films etc. having a high degree of extensibility and high elastic recovery after elongation is obtained by the melt copolymerisation of an acid of formula $HOOC{\cdot}CH_2XCH_2{\cdot}COOH$ (X = linear chain of 4–9 atoms not more than 3 being O, the remainder being hydrocarbon C atoms, any two such O atoms being separated by at least two C atoms, the hydrocarbon atoms being saturated, the chain containing $\geq$ 3 hydrocarbon C atoms as side chain substituents), e.g. sebacic acid, with terephthalic, bibenzoic, ethylene bis *p*-oxybenzoic, tetramethylene bis *p*-oxybenzoic acid and 2:6 naphthalic acid, and excess of a polymethyleneglycol of 2–6C. 30–44% of the acid components must be aromatic.

BP 711,280

Elastic products of high stick temperature are obtained if a product similar to the above but in which up to 50% of the acids may be aromatic is blended with a linear polyester prepared by melt polymerisation of at least one linear polymethylene glycol of 2–6C and one or more of the above aromatic acids, the total aromatic acid content of the blend being 40–60% by wt. of the acid components. C. O. C.

Differential Colour and/or Delustred Effects on Textiles. Courtaulds. *BP* 709,832

Cellulose acetates of the same acetyl value made by the acid process and by the methylene chloride process have different delustring characteristics and affinity for dyes. By forming yarns or fabrics from mixtures of these two types of cellulose acetate differential colour and/or delustred effects can be produced by boiling them in water and/or dyeing them. C. O. C.

Increasing the Affinity of Viscose Rayon for Acid Dyes. Phrix-Werke. *BP* 711,622

Incorporation into the rayon before or after it is formed of a polyphenol sulphide or a polyphenol sulphide of mol. wt. > 700 and a triethanolamine fatty acid ester of mol. wt. < 700 imparts the same affinity for acid dyes as is possessed by wool so that mixtures of such fibres and wool give solid dyeings in an acid dyebath. C. O. C.

Textiles and Dyes at the Frankfort Fairs (IV p. 420).
Adsorption of Water Vapour by Proteins (XII p. 427).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Starch and Pectin Zymology— Recent Results. E. Schubert. *Melliand Textilber.*, **34**, 646–648 (July), 757–758 (Aug.), 953–955 (Oct.), 1067–1069 (Nov.), 1145–1148 (Dec. 1953): **35**, 168–169 (Feb.), 381–386 (April 1954).

A review of the chemical nature, mode of action, nomenclature, classification, and structure of starch, amylases, pectinases, transglucosidases, and transdextrinases, with 281 references. H. E. N.

Critical Concentration for Micelle Formation and its Aggregation Number in Aqueous Solutions of Paraffin-chain Salts. K. Shinoda and K. Kinoshita. *Bull Chem. Soc. Japan*, **27**, 73–76 (March 1954).

A cylindrical double-layer model is adopted for the micelle. Energy changes in the formation of the micelle and the effect of an ionic atmosphere are considered, and an expression is obtained for the total energy change E_n in micelle formation. Aggregation numbers n of micelles are obtained from the condition $\partial^2 E_n/\partial n^2 = 0$, and the following expression is given for the critical micelle concentration C—

$$\log C = 3{\cdot}6 - 1{\cdot}08m + 2{\cdot}77m\dagger K - 0{\cdot}77C\dagger - 1$$

(m = No. of carbon atoms in the chain; $K = 0{\cdot}57$ for fatty acid soaps and 0·46 for sodium alkyl sulphates). C thus depends on the number of carbon atoms in the chain and not on the kind of gegenions of the same valency. The effects of added salts and of polar and non-polar oils on n and C are qualitatively discussed. W. R. M.

Solubilisation of Water in Non-polar Solvents by Detergent Mixtures. S. R. Palit and V. Venkateswarlu. *J.C.S.*, 2129–2134 (June 1954).

The solubility of water in non-polar solvents is considerably increased by binary mixtures of dodecylammonium chloride, formate, acetate, laurate, or oleate, whereas the separate constituents alone have but little effect. This increase is observed only for mixtures of a hydrophilic (e.g. dodecylammonium chloride, formate, and acetate) and a lipophilic (e.g. the laurate and oleate) detergent, but not where both the "amphiphiles" are either hydrophilic or lipophilic. These results support Winsor's theory of solubilisation (cf. *Trans Faraday Soc.*, **44**, 376, 382, 387, 390 (1948)). Freezing point data obtained with mixtures of detergents indicate little change on mixing in the average degree of association of the two individuals. It is suggested that micelle formation and solubilisation are parallel phenomena originating from the same cause, viz. the inherent tendency of soap molecules to associate either with themselves or with other molecules. H. H. H.

Loosening Rayon Cakes by Simultaneous Soaking and Deformation (VI above).

VIII— DYEING

The Forces retaining a Dye on a Fibre. F. I. Sadow. *Kolloid Zhur.*, **16**, 51–57 (1954): *Chem. Abs.*, **48**, 6702 (10 June 1954).

Bleached cotton (98·8% cellulose. 0·12% ash) was dyed with Direct Blue 200% (I), Direct Pure Blue (II), Direct Dark Blue 200% (III), Benzazurine (IV) and Direct Dark Blue KM (V) all of which are *o*-dianisidine azo dyes of formula $3{:}4CH_3O(R^1N{:}N)C_6H_3C_6H_3CH_3O(N{:}NR^2){-}3'{:}4'$ (in I R^1 and R^2 = 1-hydroxy-8-amino-3:6-disulpho-2-naphthyl; in II R^1 and R^2 = 1-hydroxy-8-amino-5:7-disulpho-2-naphthyl; in III R^1 = 2-hydroxy-1-naphthyl, R^2 = 1-hydroxy-8-amino-5:7-disulpho-2-naphthyl; in IV R^1 and R^2 = 1-hydroxy-4-sulpho-2-naphthyl; in V R^1 = 1-hydroxy-4-sulpho-2-naphthyl, R^2 = 1-hydroxy-3-sulpho-6-amino-2-naphthyl. The amount absorbed increased from I to V, e.g. in 4 hr. 100 g. of cotton at 25°c. absorbed 0·039 g. of I or 0·082 g. of V from a soln. of 0·5% of dye and 0·5% of NaCl. Thus dyes containing four SO_3Na groups were absorbed less than those containing two such groups and absorption was favoured by SO_3Na in the quinoid position to a chromophore and to a less extent by SO_3Na in the quinoid position to an auxochrome. Absorption was greater at higher temperature, e.g. 0·283 g. V was taken up at 95°c. under above conditions, and by larger amounts of NaCl; thus at 95°c. using a 0·5% solution of dye, absorption after 4 hr. was 0·088 g. and 0·318 g. of I when the bath

contained 0·5 and 20% of NaCl respectively. Absorption is greater when the number of negative groups is less and when the electrolyte concentration is greater because both these effects lower the electrostatic repulsion between dye and fibre. C. O. C.

Neutralising to improve the Handle of Acid-dyed Wool Goods. G. Sil n and L. Pakkala. *Medd. Svenska Textilforskningsinst., Göteborg*, No. 33, pp. 9 (1953): *Chem. Abs.*, **48**, 6704 (10 June 1954).

As the pH of the dyebath is decreased, so the regain of the dyed wool, and so the softness of handle, also decreases. This is specially noticeable with Cr-complex dyes applied in strongly acid baths. The regain and softness of handle can be restored by neutralising the wool. To obtain complete neutralisation and as near as possible normal regain 4 equivalents of alkali must be used for each equivalent of acid to be neutralised. C. O. C.

Plangi— Tie and Dye Work. A. Bühler. *Ciba Rev.*, **9**, 3726–3752 (June 1954).

"Plangi" a Malay term is being increasingly accepted by specialists for fabrics having resist effects produced by covering parts of the fabric by tying them with string, etc. during dyeing. The process was once familiar in Europe and is still widespread in Africa and South and South-East Asia. This article is divided into three sections dealing with the various techniques, their origin and geographical distribution and typical patterns. The creased and crimped surface of dyed fabrics imparted an effect which seems to have anticipated modern embossed styles. C. O. C.

Chrome Dyeing of Wool Piece Goods. F. Ulbig. *Melliand Textilber*, **35**, 269–271 (March), 386–388 (April 1954).

A discussion from a practical dyer's point of view under the headings— damaged wool and quality, spinning oils, size and desizing of warps, waxes used in weaving, how scoured and milled, cleanliness of wool, how carbonised and neutralised, water and steam quality, choice of dyes and method, and prevention of faults. H. E. N.

Heat-saving by Enclosure of Jigger. F. Theile. *Melliand Textilber.*, **35**, 418–419 (April 1954).

It is shown that in one case by enclosing a jigger the percentage saving in steam in the processes given is as follows— hot rinsing (2 passages, 80–90°c.) 2·6%; bleaching (10, 80–90°c.) 38·3%; boiling (5, 90–100°c.) 25·6%; overall ca. 30%. H. E. N.

Dyeing of Very Fine, Untwisted Cuprammonium Rayon. R. Schmidt. *Melliand Textilber.*, **35**, 527–528 (May 1954).

Suitable direct dyes (FBy, FH) are listed and are best applied at the boil for only 15 min. for standard colours. On Gerber machines, porcelain arms are best. For improved fastness, aftertreatment with Solidogen FFL is suggested, but, for red and bordeaux, diazotisation and development on package or Mezzera machines is necessary. H. E. N.

Azoic Dyeing of Polyamides. R. Löwenfeld. *Melliand Textilber.*, **35**, 564–566 (May 1954).

Ofna-perl Salt RRA (FH; a stabilised diazotised base) has affinity for polyamide fibres, also for other synthetic fibres and cellulose acetate, and in combination with suitable Naphtols gives yellows, reds, bordeaux, and brown. It is applied together with the Naphtol at 70°c. from a bath containing NaOH or soda ash and NaCl, but no formaldehyde, for 1 hr. The material is rinsed cold, developed in dil. H_2SO_4 at 60–70°c. for 15–30 min., and soaped. Fastness properties of dyeings are listed. They are mainly good and very good, even to such processes as thermosetting. The method is adaptable to fibre mixtures, with wool and regenerated cellulosic fibres, when Ofna-perl Salt RRA is applied together with a Naphtol or Ofnalan, then developed on the other fibre with a Fast Salt, and finally developed on the polyamide by means of acid. Full details are given. Ofna-perl Salt BBA similarly gives blues and greens. H. E. N.

Reduction–Oxidation Potential of Vat Dyes. O. Hensel. *Melliand Textilber.*, **35**, 513–515 (May 1954).

The leucopotential according to Marshall and Peters (J.S.D.C., **69**, 583 (1953)) and the "safe" potential are determined for a range of vat dyes (FH). The "safe" potential is the limit below which the vat should not be allowed to fall in order to avoid complications. For dyes difficult to apply, the "safe" potential lies at much higher values than the leucopotential. H. E. N.

Solubilised Vat Dyes on Union Fabrics of Wool and Cellulose. A. Bräutigam and H. Thumm. *Melliand Textilber.*, **35**, 516–518 (May 1954).

Recipes for the application of Anthrasol (FH) dyes are given and illustrated by 9 patterns. The fastness properties of the dyeings and the advantages of the process are listed. H. E. N.

Irgalan Hot Dyeing Method. H. R. Hirsbrunner. *Textil-Rund.*, **9**, 240–244 (May 1954).

The bath is set with 0·5–3% ammonium sulphate and 0·5–2% Irgasol DA (Gy) or 0·5–1% of 20% ammonia and is heated rapidly to 85–95°c. In 5 min. the pH of the wool will have become adjusted, and dye is added as quickly as possible. Dyeing takes place at 85–95°c. for 10 min., the temp. is then raised to the boil in 10 min. and maintained for 20–40 min. Efficient circulation is essential. The pH is 6·5–7·5. The temp. must not fall below 80°c. Shading is undertaken at the boil with the steam shut off, ¼–½% Irgasol DA being best added together with the shading dyes. Advantages claimed are savings in steam, water, and time, and the absence of any risk of bad results. H. E. N.

PATENTS

Package Dyeing of Cellulosic Textiles with Vat Dyes. ICI. *BP* 709,734

Addition of anthraflavic acid to vat dyebaths ensures that there is no undissolved vat or leuco vat dye present. C. O. C.

Dyeing Cellulose Esters, Nylon, Terylene and other Synthetic Fibres with Vat Dyes. Celanese Corpn. of America. *USP* 2,646,339

A wide range of vat dyes may be used from a bath containing water (100 parts), the leuco vat dye, an alkali metal carbonate (0·1–1·0), an alkylolamine (0·5–10·0), and a water-miscible organic swelling agent (3–25). The bath should be at 40–60°c. for 10–30 min. and then at 70–90°c. for 30–90 min. C. O. C.

Solid Prints and Dyeings or Two Colours on Mixtures of Cellulose and Cellulose Ester Fibres with Vat Dyes. Hardman & Holden. *BP* 711,154

Mixtures of vat dyes, leuco esters of vat dyes, and thiourea dioxide are applied, heated to 100°c., and then oxidised. Heating to 100°c. does not affect the vat dye leuco ester but causes reduction of the vat dye directly to the acid leuco form which is then absorbed by the cellulose ester. If the vat dyes and the parent dyes of the leuco esters are the same colour then solid dyeings or prints are obtained but if they have different colours then two-coloured effects are produced. C. O. C.

Colouring Woven Glass Fibres. General Aniline. *USP* 2,645,553

Level deep dyeings are obtained with acid, basic, direct, disperse and metal-complexes of monoazo dyes in a wide range of colours on glass fibres which have been treated with an aqueous alkali at pH 9–13, preferably a caustic alkali, in presence of a lignin sulphonic acid, at 75–100°c. for ca. 1 hr. The effect is enhanced if the fabric is simultaneously or subsequently treated with a resin, preferably a water-soluble resin, or with a compound containing an acid radical, preferably a water-soluble inorganic salt. The dyed materials are fast to washing, dry-cleaning, and rubbing. C. O. C.

Pigmentation of Viscose (VI p. 423).
Loosening Rayon Cakes by Simultaneous Soaking and Deformation (VI p. 423).
Increasing the Affinity of Viscose Rayon for Acid Dyes (VI p. 423).

IX— PRINTING

Beginnings of Calico Printing in Europe. L. A. Driessen. *Melliand Textilber.*, **35**, 389–391 (April 1954).

A short, historical review, with 22 references, describing the introduction of the "East-Indian" method from Constantinople to Holland in 1678 and thence to England, Switzerland, Germany, and France. H. E. N.

Continuous Printing of Polyvinyl Chloride. A. Franken. *Melliand Textilber.*, **35**, 563 (May 1954).
A suitable roller printing machine is described. H. E. N.

Pigment Printing. K. Craemer. *Melliand Textilber.*, **35**, 523–527 (May 1954).
A review of the principles. Though this method is sometimes stated to be applicable to any fibre and to any mixture of fibres, the degree of adhesion does depend on the type of substrate and on the construction of the fabric. Excellent reproduction is obtained in screen printing with a minimum of paste, which is important for the less absorbent materials. To avoid adhesion to the printing rollers, these are best chromium-plated. In general, washing after fixation is unnecessary. Delustrants, white or fluorescent pigments, graphite, metallic powders, and flock can be applied simultaneously, but, though pigments can be used alongside conventional classes of dyes, they are at their best when used alone. H. E. N.

Printing with Flat Screens on a Cylindrical Base. K. Prett. *Melliand Textilber.*, **35**, 419–420 (April 1954).
A machine, which can operate fully automatically with up to ten colours, is described and its advantages are pointed out. H. E. N.

Screen Printing Operations. K. Scholl. *Melliand Textilber.*, **35**, 58–61 (Jan.), 171–174 (Feb.), 276–279 (March), 391–396 (April 1954).
The technical accessories available are given in considerable detail, including the names of their manufacturers. Many photographs and diagrams illustrate the construction of tables, sticking-down machines, tearing-off machines, table washers, frames, gauzes, pattern and screen preparation, a machine for testing the length of life of varnished screens, agers, the mechanisation of processes and screen printing machines, including one for the printing of cotton socks. H. E. N.

PATENTS

Printers' Wash Blanket. Dewey & Atmey Chemical Co. *BP* 711,548–9
A wash blanket of long life and high colour carrying capacity has its working surface formed of a material made from synthetic fibres. This layer adheres to the backing by means of a cushioning layer made of an elastically deformable material. C. O. C.

Pigmented Prints, Coatings, etc. on Fibrous Materials. Basf. *BP* 709,954
Supple, waterproof friction-resistant prints are obtained by use of an emulsion consisting of a water-insoluble organic solvent of b.p. $> 75°$C. dispersed in an aqueous dispersion of a water-insoluble polymer, a water-soluble protective colloid and a cross linking agent containing >1 reactive group capable of reacting by addition with compounds containing reactive H atoms. The cross linking agent can react with the colloid but not with the polymer. After the emulsion has been applied, it is dried and baked to effect cross linking. Suitable cross linking agents are polymethylene diethyleneimine or poly*iso*cyanates and suitable colloids include casein and polyvinyl alcohol. C. O. C.

Figured Effects on Cellulosic Fabrics. Bleachers' Assocn. *BP* 709,735
Prints produced by aqueous emulsions or organic solvent solution of thermohardening synthetic resins will, after hardening, resist the organdie process. The printed portions remain soft and supple in contrast to the crisp and translucent organdie effect produced on the unprinted areas. If desired the emulsion may contain a pigment and in addition a non-resinous *N*-organic compound containing at least one aliphatic chain which when heated renders cellulose water repellent may either be incorporated in the emulsion or applied separately to selected areas of the fabric. C. O. C.

Printing Organic Derivatives of Cellulose. Celanese Corpn. of America. *BP* 710,607
Solutions of dyes in aqueous alcohols are made into printing pastes by thickening with an alkylamine alginate. C. O. C.

Transfer Paper and Transfers. R. S. Colour Works. *BP* 711,723
The design on the transfer is coated by screen printing with cellulose acetate or nitrate, the uncoloured areas of the transfer remaining uncoated. When the transfer is applied to a ceramic blank there is no superfluous cellulosic film to be removed before firing. C. O. C.

Ornamental Coatings. A. Vogt. *BP* 710,751
Irridescent colour effects of a purity and brilliance hitherto unobtainable are produced by using as a coating at least one metal layer which is light-absorbing, light-reflecting, partly permeable to light and unclouded and at least thereon another layer which is absorption-free, has a refractive index greater than that of air, is unclouded and consists of a metal compound resistant to chemical and mechanical action. The layers should have a thickness of the order of the wave length of light so that interference effects occur by reflection of the incident light at the boundary surfaces of the layers. In the case of metals its own surface may provide the metal layer. At least one layer is applied by high vacuum evaporation. C. O. C.

Diazotype production of Photomechanical Printing Plates. Kalle & Co. *BP* 711,808
Modification of *BP* 699,413 (J.S.D.C., **70**, 33 (Jan. 1954)). Diazo compounds derived from sulphonic or carboxylic acids of *o*-diazophenols of the benzene series (*o*-quinone diazides) and having the constitution of esters or amides of these acids are used to replace wholly, or in part the diazo compounds derived from 2-diazonaphthol-(1) or 1-diazonaphthol-(2). These new diazo compounds are insoluble in water but soluble in organic solvents. They produce red-brown images on a pale yellow ground. C. O. C.

Protecting Colour Photographs exposed to High Humidities against Fading and Staining. Pavelle Color. *USP* 2,647,057
The photographs are given a final rinse in a dilute aqueous solution of an alkali, preferably borax, and an antistaining agent, preferably sodium formaldehyde-bisulphite. C. O. C.

Solid Prints and Dyeings or Two Colours on Mixtures of Cellulose and Cellulose Ester Fibres with Vat Dyes (VIII p. 424).

X— SIZING AND FINISHING

Calendering of Circular Fabrics. E. Meyer. *Melliand Textilber.*, **35**, 260 (March), 366–367 (April 1954).
Frictioning is carried out with the help of an endless felt. Tables give the expected shrinkage in length (5–12%) and in width (4–12%) of these fabrics during wet processing, and the width at which these fabrics should be batched when untreated or when wetted. H. E. N.

Simili-mercerisation. Anon. *Melliand Textilber.*, **35**, 560–562 (May 1954).
This process consists in passing the wet cotton cloth through a heavy, hydraulic calender between a cotton and a steel bowl, the latter being heated to up to 300°C. The process reduces the swelling of the fibres and is thus somewhat fast to washing, giving a lustrous finish imitating that produced by mercerisation. The process is especially suitable for combination with chasing and for heightening the lustre of goods already normally mercerised. If the fabric is dyed, fast dyes are required. H. E. N.

Effect of Oxidation and Reduction Processes upon the Properties of Wool. E. Sörvik. *Medd. Svenska Textilforskningsinst., Göteborg*, No. 35, 15 pp. (1953): *Chem. Abs.*, **48**, 6703 (10 June 1954).
Treating wool with 0·2N-$NaHSO_3$ at pH 1–5 for 2 min. did not affect its alkali solubility, frictional properties or felting power but did lower the modulus of elasticity by 3–6%. Oxidation with $KMnO_4$ was slow at pH 4 but quick at pH 2. Pretreatment with alcoholic KOH accelerated the oxidation. With 0·05N-$KMnO_4$ at pH 1, the modulus of elasticity and speed of felting were reduced but the alkali solubility and frictional properties were increased. Wool treated first with $KMnO_4$ and then with $NaHSO_3$ at pH 2 looked unaffected but its sensitivity to alkali was greatly increased, even being affected by distilled water at pH 6. Depending upon the intensity of the oxidation, reduction resulted in there being minor swelling of the scale edges to gelatinisation of the outer parts of the fibres. Moderate oxidation-reduction treatment affected neither the handle nor the frictional properties but with intense oxidation handle was badly affected; alkali solubility was less than that of wool which had only been oxidised. The $NaHSO_3$-induced decrease in modulus of elasticity was proportional to the

time of oxidation. Rate of felting was significantly lowered by treatment with 0·5N-$KMnO_4$ at pH 1 for 2 sec. followed by 0·2N-$NaHSO_3$ for 2 min. C. O. C.

Shrink-resisting of Wool. G. Strauch. *Melliand Textilber.*, **35**, 530–532 (May 1954).
A review with many references. H. E. N.

Finishing Mixtures of Wool and Man-made Fibres. C. S. Whewell. *Melliand Textilber.*, **35**, 528–530 (May 1954).
A discussion of preparation, scouring, and setting. Care must be taken in knotting, as the weave does not close up as with all-wool material. Less heavily built scouring machines are required for fabrics containing a large proportion of rayon staple. H. E. N.

PATENTS

Mercerising and Calendering Cotton Cloth to impart Lustre. Cluett, Peabody & Co. *USP* 2,646,341
A permanent silky appearance and handle is imparted to cotton cloth by impregnating with mercerising lye, lightly rinsing and then heavily calendering, these last steps being repeated several times. Throughout the treatment the cloth is held to normal width. C. O. C.

Crease-resisting Finish. Monsanto. *USP* 2,646,340
Cellulosic textiles are partly esterified or etherified without swelling the fibres more than would water. This is preferably done with formic acid. They are then impregnated with an aqueous solution of an aldehyde-urea and/or -melamine precondensate or other thermosetting condensates, dried and baked. This imparts excellent crease- and wrinkle-resistance with no loss of tensile strength. C. O. C.

Imparting Resistance to Shrinking and Felting of Fabrics containing Wool. Monsanto. *BP* 711,476
The fabric is treated with an acidic aqueous colloidal solution of a partly polymerised methyl ether of a methylol melamine condensate containing at least 2–8 mol. of combined HCHO and at least 2 mol. of combined methanol per mol. of melamine, the solution also containing acetic, hydroxyacetic or formic acid. The fabric should pick up 3·5–8·0% of its wt. of the condensate. Finally the impregnated fabric is heated to 200–325°C. to insolubilise the condensate. There is no yellowing, tendering, or harshening of the handle and exceptional resistance to shrinking and felting is obtained. C. O. C.

Resin Finish for Cellulosic Fabrics. Monsanto. *BP* 711,477
Cellulosic fabrics treated as in *BP* 711,476 (above) but with 1–12% of the condensate are given dimensional stability and a durable stiff finish. The treatment can also be used to fix dyeings which normally bleed in hot water. C. O. C.

Imparting Flame Resistance to Cellulosic Textiles. American Cyanamid Co. *BP* 711,699
Modification of *BP* 671,699 (J.S.D.C., **68**, 328 (1952)). The materials are impregnated with 1 part of (A) a mixture of 1 part of an oxide of Sb, Bi, Sn or Al, and 0·6–20·0 parts of a thermoplastic substance containing $\leq$ 20% by wt. of combined halogen and rupturing at C–Hal bonds when heated and 0·2–8·0 parts of (B) a water-soluble salt of an aminophosphoric acid having an amino N atom directly attached to P, of m.p. $<$ 200°C. and whose cations contain N and no metal, or a guanidine or guanyl-urea salt of an oxygen-containing polyacid of phosphorous whose P has valency 5. These ingredients are applied in the form of at least one aqueous liquid containing some or all of A and B and not more than two separately applied aqueous liquids containing some of A and B respectively. The material is dried, baked and washed. After washing the fabric should contain 10–75% of its initial dry wt. of the flame-resisting composition. C. O. C.

Impregnating Cellulose Fibres with Sericeous Material. T. C. Whitner. *USP* 2,646,372
The cellulose fibres are impregnated with silk dissolved in an aqueous solution of tetra-alkylol ammonium hydroxide-copper complex and a tetra-alkylol ammonium hydroxide and then washed with an acidic aqueous solution which yields water-soluble salts with the copper and tetra-alkylol ammonium hydroxide. C. O. C.

Fusible Interlining Fabric for Collars, etc. Kendall Co. *USP* 2,646,374
Cotton cloth coated with a mixture of separately-polymerised polyvinyl chlorides of high ($>$ 20,000) and low (5,000–16,000) mol. wt. is used as the interlining for fusing to the surface fabric of collars etc. The combined fabric is permeable to perspiration and liquids while retaining its stiffness after repeated washings and ironings. C. O. C.

Microbiology of Cellulosic Textiles (VI p. 422).
Increasing the Affinity of Viscose Rayon for Acid Dyes (VI p. 423).
Starch and Pectin Zymology— Recent Results (VII p. 423).
Figured Effects on Cellulosic Fabrics (IX p. 425).

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Effect of Free Carboxyl Groups on the Decomposition of Cellulose on Heating. T. N. Kleinert and W. Wincor. *Textil-Rund.*, **9**, 201–205 (April 1954).
Cellulose pulp was treated with 0·1N-HCl to liberate all carboxyl groups and was then washed free from mineral acid. A portion was treated with 0·04N-NH_4OH and washed, another with 0·04N calcium acetate and washed. On heating for 48 hr. at 105°c., the degree of polymerisation (D.P.) of the cellulose containing free carboxyl groups decreased by 15·4%, that of the cellulose containing $COONH_4$ groups by 14·5%, and that of the cellulose containing COO^-a groups by 8·5%. Comparing the effect of heating at 105°c. for 60 hr. with that for 2 hr. on four samples of pulp (beech and fir), the viscosity of Ca-free samples was reduced by 17·6–28·3%, that of samples saturated with Ca by only 1·9–5·5%. Such a difference is stated to occur also on exposure to light. The carboxyl groups in a viscose rayon were similarly liberated and half the sample was converted into the Ca salt by means of water of 8° (German) total hardness. Both samples were treated with H_2O_2 soln. (1·6 g./litre), hydroextracted to 180% of their dry wt., and heated at 105°c. In the first 30 min. of heating, the No. of free carboxyl groups increased rapidly in both samples. The D.P. decreased with time of heating, less rapidly with the Ca-containing specimen. The degree of whiteness was at a max. just after 1 hr., and then fell, slightly less rapidly with the Ca-containing specimen. H. E. N.

***p*-Hydroxybenzyl Ethers as Lignin Models— II.** H. Mikawa. *Bull. Chem. Soc. Japan*, **27**, 53–59 (Feb. 1954).

PATENTS

Sized Paper. American Cyanamid Co. *BP* 711,404
Sized paper containing, if desired, an alkaline filler such as calcium carbonate to the extent of 2% to 30% by weight of the paper, is made by preparing a dilute aqueous suspension of cellulosic papermaking fibres, adding to it 0·1–5%, preferably 0·1% to 3%, of the dry weight of the fibres, of a water-soluble amide salt of a higher fatty acid-alkylenepolyamine condensate, then mixing in the finely-divided alkaline filler, forming paper, and heating it to dry it and develop the sizing properties of the amide. S. V. S.

Organosilicon Compounds for imparting Wet Strength and Resistance to Ink Penetration to Paper. Cowles Chemical Co. *USP* 2,646,373
The fibres are heated either before or after they have been formed into paper with the alkaline hydrolysate of *n*-buytl, mixed amyl or benzyl trihalogenosilane at pH 7, drying and baking. C. O. C.

Transparent Paper. R. E. Parmentier. *USP* 2,646,369
A composition which makes paper transparent consists of mineral oil (10–35 vol. %), toluene (4–10) and CCl_4 (55–80). C. O. C.

Transfer Paper. National Cash Register Co. *USP* 2,646,367
A transfer sheet is coated with a hydrophobic composition containing a colourless oil carrying a colour-reactant material. The oil is carried in a low polar wax binder. The sheet is for use on paper sensitised by particles of acid-like, colourless inorganic materials which give an adsorption colour reaction when the colour reactant in the transfer sheet is transferred to this second sheet. C. O. C.

Water-repellent Non-fibrous Cellulosic Material. American Cyanamid Co. *USP* 2,646,368

The material is treated with an aqueous solution of a water-soluble thermo-setting urea-formaldehyde condensate modified by reaction with a compound of formula $NH_2(CH_2)_nOSO_3X$ (n = 1–6; X = H, Li, Na, K, NH_4, or H in combination with a water-soluble tertiary amine) which acts as a binding agent (which itself has water-repellent properties) for a water-repellent top coating. C. O. C.

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Adsorption of Water Vapour by Proteins. H. B. Dunford and J. L. Morrison. *Canadian J. Chem.*, **32**, 558–560 (May 1954).

Bull's isotherms for the adsorption of water vapour by proteins are fitted by the Brunauer–Emmett–Teller equation for the range of relative vapour pressures 0·05–0·5. The Harkins–Jura equation is applied to Bull's data, and in most cases linear plots are obtained over the range 0·5 or 0·6 to 0·95. Nylon gives linear plots over the range 0·7–0·95. The amount of water vapour in a monomolecular layer is calculated from both equations and good agreement obtained. It is suggested that a film at least two molecules thick is formed, the upper layer being condensed and occupying the same surface area as the underlying monomolecular layer, the same number of adsorption sites being involved. The fact that nylon obeys the H.–J. equation over a smaller pressure range may be due to the larger water-repellent hydrocarbon spacings between peptide links hindering condensed film formation. W. R. M.

Some Factors influencing the Orientation of ε-Amino Groups in Monolayers of Proteins and Amino Acid Polymers. J. T. Davies. *Biochem. J.*, **56**, 509–513 (March 1954).

The potentials of monolayers of various proteins and amino acid polymers, including a new synthetic amphoteric amino acid polymer, have been measured at the interfaces air–water and oil–water, at pH values 2, 6·8, and 13. With this new polymer (poly-1:1:2-L-lysyl-L-glutamyl-L-leucine) all the phenomena shown by protein films can now be reproduced. Other polymers studied were poly-L-lysine, poly-DL-leucine, poly-1:1-γ-methyl-L-glutamyl-DL-phenylalanine, and poly-1:1-DL-lysyl-L-glutamic acid. At pH 13 the unionised ε-amino groups of the lysine residues tend to enter the non-aqueous phase, especially at the air–water interface when the neighbouring amino acid residues in the peptide chain are favourable. P. G. M.

XIII—RUBBER; RESINS; PLASTICS

Surface Chemistry of High Polymers. III—Some Relationships between the Monolayers of Non-electrolytic Linear Polymers. H. Hotta. *Bull. Chem. Soc. Japan*, **27**, 80–84 (March 1954).

Measurements of surface pressure, surface potential, and interfacial pressure are made with films of polymethyl methacrylate, undissociated polymethacrylic acid, polyacrylonitrile, and aminocaproic acid polymer on water. Surface moments and areas at which reliable surface moments can be obtained are interpreted in terms of the orientation of the C = O bond at the interface. Flexibility of films can be measured not only from surface pressure but also from the time for perfect spreading, the largest area from which the reliable surface moment can be obtained, or the number of atoms in the main chain of the statistical kinetic unit. The effect of hydrolysis of the aminocaproic acid polymer on its surface film is examined. W. R. M.

Surface Chemistry of High Polymers IV—The Monolayer of Polymethacrylic Acid and its Copolymers with Diethylaminoethyl Vinyl Ether at the Air–Water Interface. T. Isemura, H. Hotta, and S. Otsuka. *Bull. Chem. Soc. Japan*, **27**, 93–97 (March 1954).

Surface moments were constant up to pH 4, and then fell rapidly to zero between pH 4 and 5·5. Stable films could not be obtained at pH > 5. Surface pressure decreased with increasing pH. These results are discussed in terms of Katchalsky's interpretation of the shape of polymer molecules and degree of ionisation. It is concluded that all the side-chains of the polymer are immersed in the aqueous phase, that the degree of ionisation of amino groups may be about 20% even at its maximum, and that the isoelectric point of the copolymer at the interface occurs at about pH 5 for the aqueous phase. W. R. M.

Colouring Agents for Elastomers and their Packaging (IV p. 422).
Polyacrylonitrile Fibres, Films, etc. (VI p. 423).
Elastic Linear Copolyester Fibres, Films, etc. (VI p. 423).

XIV—ANALYSIS; TESTING; APPARATUS

Auxiliary Products—Testing Resistance to Hardness of Water. DIN 53,905. *Melliand Textilber.*, **35**, 551–552 (May 1954).

5 ml. of a 5% soln. of the product to be tested (I) in dist. water is diluted to 50 ml. with water of 20° German hardness (17° due to $CaCl_2$, 3° due to $MgSO_4$) and is shaken ten times, the temp. being 25° ± 2°c. The test is similarly carried out with 2·5, 1·25, 0·65, and 0·33 ml. of I, and the whole is repeated with water of 30° (25·5° + 4·5°) and 40° (34° + 6°). After 1 hr., it is visually determined whether and at which concn. a ppt. or turbidity appears. Products are classified as resistant to hardness when no ppt. or turbidity is formed, as conditionally resistant to hardness when only at low concn. and only at 30° or 40° pptn. and at lower hardness turbidity occur, and as not resistant to hardness when at all five concn. and at all three degrees of hardness ppt. are formed. H. E. N.

Auxiliary Products—Standard Methods of Test. G. Schwen. *Melliand Textilber.*, **35**, 545–547 (May 1954).

The considerations leading to DIN 53,905 (see above) are given, and some relevant experiments are reported H. E. N.

Evaluation of Detergency of Auxiliary Products. I—Standard Soiled Samples. E. Götte. *Melliand Textilber.*, **35**, 534–535 (May 1954).

Impurities in textiles were reviewed in Part I (cf. J.S.D.C., **70**, 97 (Feb. 1954)), and this review, with 51 references, covers substrates, pigments, and oils used in preparing soiled samples for detergency tests. H. E. N.

Auxiliary Products—Testing Foaming Power and Persistence of Foam. DIN 53,902. *Melliand Textilber.*, **35**, 548–549 (May 1954).

The test can be carried out at 25 ± 2°c., 40 + 2°c on any other agreed temp. 200 ml. of a soln. (usually 0·2% of the auxiliary product (I) is placed in a standard 1000-ml. measuring cylinder (DIN 12,680) and agitated with 30 strokes in 30 sec. from a special plunger, consisting o a Plexiglas disc, 55 mm. in diameter, perforated with 40 holes of 4·5 mm. diameter, and a stainless steel rod, 500 mm. long and 5 mm. in diameter. The volume of foam formed is measured in ml. after 1, 5, and 10 min, and expressed as a percentage of that similarly produced by a 0·2% soln of pure sodium oleate in *distilled* water after standing fo 1 min. The report must state the concn. of I and the temp. employed and must record the three results using dist. water and three more using water of 10° German hardness (8·5° due to Ca, 1·5° due to Mg) or water of a given greater hardness as solvent for I. H. E. N.

Papyrography of Organic Dyes. K. H. Kludas. *Chem. Tech.* (Berlin), **6**, 39 (1954): *Chem. Abs.*, **48**, 6326 (10 June 1954).

By use of Zimmermann's paper disc method (*Chem. Abs.*, **47**, 9205 (1953)) it was postulated that the R_f valu is mainly a function of the speed of development (v) as long as the development phase (EP) and temperature (t) are kept constant: $R_f = F(v)EPt$. This equation is of general validity: adsorption phenomena are readily explained. During the work coloured ions were excluded. Seven food dyes, allegedly single dyes, were used, but only two proved to be homogeneous, the other five yielding a mixture of red, purple, violet, and blue bands in the papyrograms. The development chambers used were the dome-type desicca ors described by Zimmermann and Nehring (*Chem. Abs.*, **46**, 2952 (1952)). Defatted wool yarn at the centre of the circular filter papers was valuable; 0·01–0·02 ml. of a 10% dye soln. was used. Development was with water. R_f values obtained from the 7 dyes and those from the separated component dyes are tabulated. C. O. C.

Chromatographic Analysis of Dyes in Foods. G. Panapoulos and J. Mégaldoikonomos. *Chim. anal.*, **36**, 68–9 (1954); *Chem. Abs.*, **48**, 6609 (10 June 1954).

Description of a method which has proved satisfactory in practice. C. O. C.

Determination of Moisture in Textiles. L. T. Muus and R. W. Asmussen. *Trans. Danish Acad. Tech. Sci.*, **5**, (1952); *Textil-Rund.*, **9**, 220 (April 1954).

By measuring the dissipation factor of a condenser at 100 kilocycles/sec., the moisture content of woven fabric can be determined within ± 0·23%. H. E. N.

Differentiation of Nylon and Perlon. A. Wöllhaf. *Melliand Textilber.*, **35**, 533 (May 1954).

Contrary to Reif (cf. J.S.D.C., **69**, 272 (1953)), boiling Sesolvan NK (198°c.) dissolves both fibres, but if used at 173–175°c. the test is satisfactory. Nylon remains insol., whereas Perlon gives a soln., which sets to a gel on cooling. Heat-set Perlon dissolves less readily, requiring 10 min. to dissolve at 180°c. H. E. N.

Microscopic Differentiation of Nylon and Perlon. W. Pekar. *Melliand Textilber.*, **35**, 532–533 (May 1954).

Under a microscope, a soln. of chloral hydrate (3·8 g. in 2 c.c. water) is seen to dissolve nylon quickly, but Perlon only slowly. A weaker soln. (2·5 g. in 2 c.c.) does not dissolve nylon, which swells strongly, but Perlon does dissolve slowly. After treating for 30–45 sec. in a mixture of phenol (10 g.), lactic acid (75%, 10 g.), glycerol (95%, 20 g.), and water nearly saturated with Sirius Blue or Cotton Blue (22 c.c.), and rinsing with water, nylon is hardly dyed and otherwise practically unchanged, but Perlon is deeply dyed, strongly swollen, and even partly dissolved. H. E. N.

Identification of Polyvinyl and Polyacrylic Fibres and Finishes. H. Rath and L. Heiss. *Melliand Textilber.*, **35**, 536–540 (May 1954). H. Rath. *Textil-Rund.*, **9**, 196–201 (April 1954).

Splitting off of HR from polyvinyl deriv. $(CH_2{\cdot}CHR)_n$ by means of alkaline reagents becomes more difficult in the order R = Cl (copolymerised < chlorinated < normal polyvinyl chloride) < OR′ < OH < O·CO·R′. As the residue is a coloured polyene, advantage can be taken of this reaction for purposes of identification. A drop of the polymer dissolved in tetrahydrofuran (dye can be removed by adsorption on alumina) is applied to filter paper, and the solvent removed. The paper is treated for 20 min. in refluxing methyl alcohol containing a little Na, and rinsed with much water. Polyvinyl chloride copolymer is converted into intensely yellow to red-brown polyenes, black-brown after prolonged treatment. To obtain polyenes from normal or chlorinated polyvinyl chloride, Na in butyl alcohol is required. With polyvinyl alcohol or acetate, finely powdered sodamide in refluxing benzine (b.p. 110–140°c.) for 1 hr. is used, when a brown coloration is produced. Alternatively, thionyl chloride is added to polyvinyl alcohol, warming to begin reaction, but cooling later, until a soln. is obtained. This is at first yellow, but becomes black-brown giving an almost black ppt. Phenyllithium, which requires working under nitrogen, can also be employed to convert polyvinyl deriv. into variously coloured polyenes. This reagent is used to convert polyacrylates into colourless polyvinyl-ββ-diphenylcarbinols—

$$-COOC_2H_5 \rightarrow -C(C_6H_5)_2OH$$

which give an intense wine-red soln. in H_2SO_4 (yielding a blue ppt. on dilution with water), an intensely wine-red soln. in thionyl chloride, and an intensely green colour on heating with anhyd. $ZnCl_2$ for 1 hr. at 120°c. These colours are due to polyenes formed by loss of water. Phenyllithium also reacts with polymethacrylates yielding a ββ-diphenylcarbinol, which dissolves in H_2SO_4 with a red colour, being reprecipitated unchanged on dilution with water. The alkoxy groups of polyvinyl ethers and polyacrylic esters can be determined qualitatively by using an aq. suspension of silver 3:5-dinitrobenzoate in the Zeisel apparatus and isolating the alkyl 3:5-dinitrobenzoate formed. Polyacrylonitrile can be identified by its solubility in dimethylformamide and by its affinity for acid dyes in presence of cuprous ions. Full practical details of these reactions are given, together with theoretical explanations. H. E. N.

Independent Determination of Cysteine and Cystine in Proteins. R. D. Strickland, E. L. Martin, and J. L. Riebsomer. *J. Biol. Chem.*, **207**, 903–910 (April 1954).

The method is based on the observation that formaldehyde condenses quantitatively with cysteine under conditions that do not affect cystine. Following condensation, cystine is precipitated as the cuprous mercaptide, while cysteine remains in solution as thiazolidinecarboxylic acid. The method was tested with the free amino acids, derivatives of the acids, and with ovalbumin. The deviation range of the method for cysteine within 95% confidence limits is ± 2·1%, while for cystine it is ± 3·0%. P. G. M.

Determination of Monoamino Monocarboxylic Acids by Quantitative Paper Chromatography. A. R. Kemble and H. T. Macpherson. *Biochem. J.*, **56**, 548–555 (April 1954).

Paper partition chromatography has been applied to the separation of the neutral amino acids isolated by ionophoresis. The method has particular value for the free amino acids to be found in plant extracts. Determination of the separated amino acids eluted from the chromatograms depends on the evolution of CO_2 in a Warburg respirometer following oxidation with chloramine-T. The following degrees of accuracy have been achieved in the analysis of made-up mixtures of amino acids within the optimum range for each amino acid of 0·08–0·25 mg. N: leucine + *iso*leucine, valine, proline, alanine, and glycine (100 ± 3%); *iso*leucine (99–93%); leucine (106–97%); threonine (in absence of hydroxyproline), serine, phenylalanine (100 ± 5%); tyrosine (in absence of tryptophan) (100 ± 8%); methionine (105–90%). P. G. M.

Continuous Direct Photometry of Dyed Materials in Filter Paper with special reference to the Estimation of Proteins Separated by Electrophoresis. E. M. Crook, H. Harris, F. Hassan, and F. L. Warren. *Biochem. J.*, **56**, 434–444 (March 1954).

An apparatus is described for the continuous photometry of dyed materials in filter paper, which has been successfully employed for the estimation of proteins separated by electrophoresis. The applicability of Beer's law to the absorption of light by dyed protein in an immersed filter paper was tested experimentally. It was found that, outside a very restricted range, large deviations occur. A method of calibration is described by which the deviation from Beer's law may be estimated and compensated for. P. G. M.

Testing the Ease of Removal of Carding or Combing Oils by Washing. DIN 53,904. *Melliand Textilber.*, **35**, 550–551 (May 1954).

A certain amount of the oil to be tested is dissolved in a CCl_4 soln. containing some Ceres Violet BRN and is applied to a pure wool, lightly milled flannel, which is then washed by means of a soln. of Na_2CO_3 (13 g./litre). The ease of removal of the oil is judged visually by the amount of the oil-soluble dye remaining in the pattern. H. E. N.

Colorimeter for Pyrotechnic Smokes. I. Nimeroff and S. W. Wilson. *Bur. Stand. J. Res.*, **52**, 195–199 (April 1954).

A direct-reading tristimulus photoelectric colorimeter has been designed to measure the colour of smokes. The colorimeter incorporates three modified commercial photometers which use electron multiplier photocells, and the smoke chamber (1 yd. cube) is sufficiently large to avoid end effects. Design details are given for the glass filter, particularly the C.I.E. x-function, which is bimodal. Comparison has been made with the Munsell book of colour, but since the smoke gives higher chroma values than the Munsell book there is some uncertainty in the hue steps. W. J. M.

Determination of Formaldehyde bound in Cellulosic Textiles. T. N. Kleinert and J. Bauer. *Melliand Textilber.*, **35**, 374 (April 1954).

The sample (30 mg.), the dry wt. of which has been determined separately, is dissolved in 5 c.c. $ZnCl_2$ soln. (saturated at room temp.) by heating at 120–130°c. for 5 min. in a current of nitrogen. Heating is continued, but 15–20 c.c. water is added dropwise. The formaldehyde is distilled in the steam in ca. 30 min. into a receiver containing a little water and is estimated by means of chromotropic acid in 72% H_2SO_4. The distillate is practically free from furfural and ω-hydroxymethylfurfural. H. E. N.

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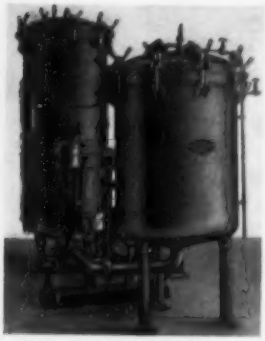

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SITUATIONS VACANT (see also page xxxiii)

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Review of Textile Progress

Volume 4

Compiled and published jointly by the Textile Institute
and the Society of Dyers and Colourists

Editors W J HALL A.R.C.S B.Sc C J W HOOPER PH.D D.I.C A.R.C.S Miss C E M JONES M.A

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FORTHCOMING MEETINGS OF THE SOCIETY — *continued from page* xii

Wednesday, 23rd February 1955
MIDLANDS SECTION. *The Classification of Dyestuffs by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. Kings Head Hotel, **Loughborough.** 7 p.m.

March 1955
LONDON SECTION. The London Lecture. Details later.

Friday, 4th March 1955
MIDLANDS SECTION. MIDLANDS SECTION DINNER. Kings Head Hotel, **Loughborough.** 7 p.m.

Wednesday, 9th March 1955
NORTHERN IRELAND SECTION. Film Evening. (Joint Meeting with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th March 1955
MIDLANDS SECTION. *The Diffusion of Vat Dyes into Cellulose.* R. H. Peters, Esq., Ph.D., F.S.D.C., and T. Watson, Esq., Ph.D. (Dr. Peters lecturing). Gas Theatre, **Nottingham.** 7 p.m.

Wednesday, 6th April 1955
MIDLANDS SECTION. Paper by G. H. Lister, Esq., B.Sc., Ph.D. (Subject later) (ANNUAL GENERAL MEETING at 6.30 p.m.). Kings Head Hotel, **Loughborough.**

Thursday, 21st April 1955
MIDLANDS SECTION. *Some Experiences of a knitted-goods dyer.* A. W. Carpenter. (Joint Meeting with the Textile Institute Kidderminster Section). Carpet Trades Canteen, Mill Street, **Kidderminster.** 7 p.m.

SITUATIONS VACANT AND WANTED *etc*

Replies may be addressed "Box —, SOCIETY OF DYERS AND COLOURISTS," DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKS., where all communications relating to these Advertisements, which are treated in strict confidence, should be addressed.

The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to THE SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKS.

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DYEING and Finishing concern in the West of Scotland require a capable man experienced in the application of ester vat, vat and azoic dyestuffs to cotton piece goods. The post offers considerable scope for a person with the necessary ability and enthusiasm. Reply giving full particulars to Box V51.

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Chapman, E. D., formerly of 55 Parkfield Road, Northenden, Manchester, to 221 Slade Lane, Levenshulme, Manchester

Desai, B. R., Dyeing, Bleaching and Finishing Master, formerly of Dahi Nivas, Maninagar, Ahmedabad 8, India, to The Sidhpur Mills Co. Ltd., Sidhpur (N. Gujarat), India

Drake, S. T., formerly of 23 Baronsmead, Whitkirk, near Leeds, to 11 Dorchester Road, Fixby, Huddersfield.

Ellse, B. L., formerly of 31 Coniston Grove, Heaton, Bradford, to High Barn, Manor Park, Burley-in-Wharfedale

Evans, D. G., formerly of The Bungalow, Oakenroyd Hill, Rochdale, to 8 Woodgate Avenue, Bamford, Rochdale

Foltz, T. R., formerly c/o Philadelphia Textile Institute, School House Lane and Henry Ave., Philadelphia 44, Pa., U.S.A., to c/o Lockport Felt Company, Newfane, N.Y., U.S.A.

Glasman, I., formerly of 59 Dudley Court, Upper Berkeley Street, London W1, to Flat 406, Russell Court, Woburn Place, London WC1

Gupta, P. K. Sen, formerly of 21 Burns Street, Levenvale, Alexandria, Dumbartonshire, Scotland, to Jagudas Para Lane, Hooghly, West Bengal, India

Hovland, Hans, formerly of 14 Rawson Road, Bradford, to 60 Meadow Lane, Loughborough

Huddlestone, P., formerly of 211 Halifax Road, Birchencliffe, Huddersfield, to 90 Micklehurst Road, Micklehurst, near Mossley, Manchester

Johnston, Miss M., formerly of Ashfield Print Works, near Dunblane, Perthshire, to Standfast Dyers & Printers Limited, Caton Road, Lancaster

Jowett, F., formerly of "Corrour", 8 Nab Wood Mount, Shipley, Yorks., to c/o The Lawns, Ashcott, near Bridgwater, Somerset

Madaras, Dr. G. W., formerly of Lyddon Hall, Virginia Road, Leeds 2, to 22 Blenheim Road, Manningham, Bradford 8

Myers, W. H., formerly of 389 Lower Heidelberg Road, Heidelberg N22, Victoria, Australia, to 33 Ryan Street, West Bowling, Bradford

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Nixon, I. G., formerly of Adriaan Goekooplaan, 105, Flat Gebouw Catsheurel, The Hague, Holland, to Goetlijfstraat, 94, The Hague, Holland

Robinson, G., formerly of Carpet Trades Ltd., Mill Street, Kidderminster, to "Redcroft", 18 Western Road, West Hagley, near Stourbridge, Worcs.

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Royer, G. L., formerly of American Cyanamid Company, Bound Brook, New Jersey, to American Cyanamid Company, 30 Rockefeller Plaza, New York 20, New York, U.S.A.

Shenton, A., formerly of 453 Huddersfield Road, Waterhead, Oldham, Lancs., to Loughborough Dyeworks, Whitegate Mill, Nottingham Road, Loughborough

Travis, F., formerly of 2 Davenport Flats, Davenport Road, Vreoehoek, Cape Town, South Africa, to 8 Parkchester Avenue, Pinelands, Cape, South Africa

Walker, R. D., formerly c/o Ciba Co. Pty. Ltd., 119 Victoria Street, Christchurch, to 10 Denman Street, Sumner, SE3, Christchurch, New Zealand

Warren, W., formerly of Avenue Cottage, Alexandria, Dumbartonshire, to Rosshead, Alexandria, Dumbartonshire

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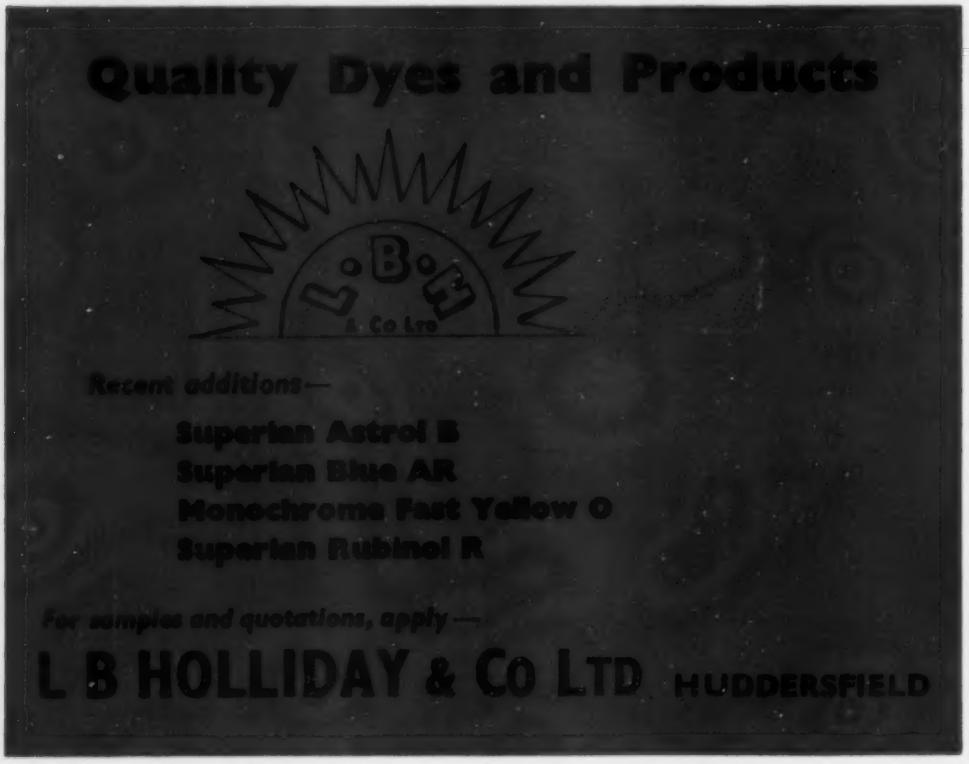

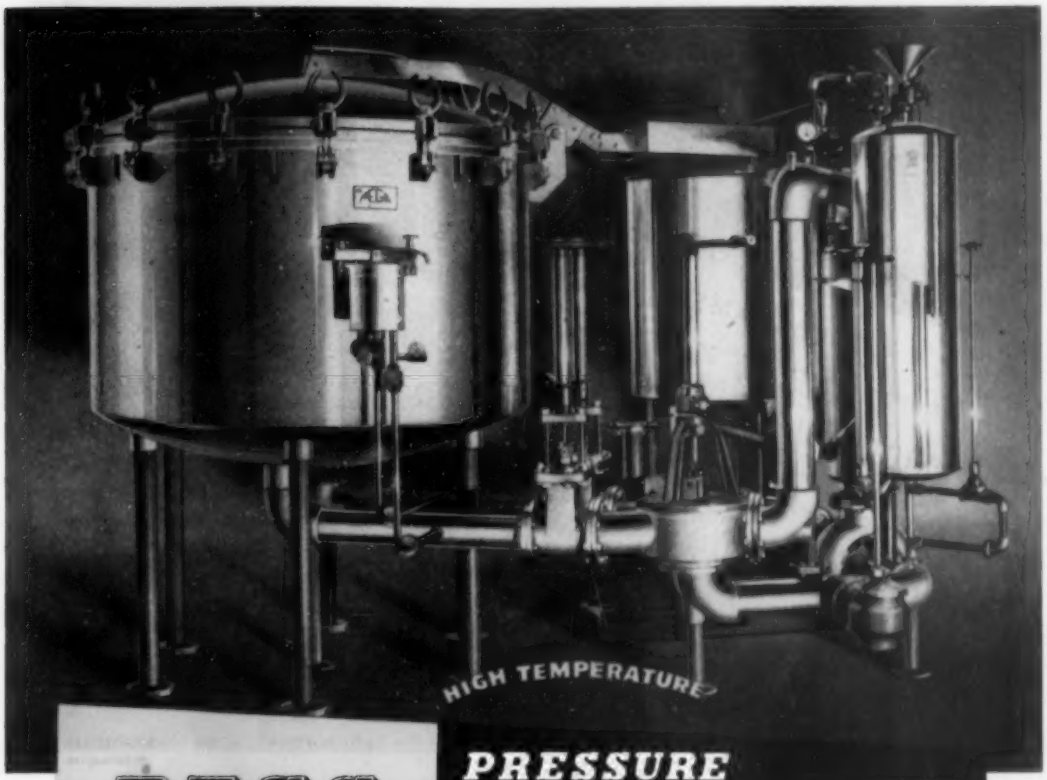

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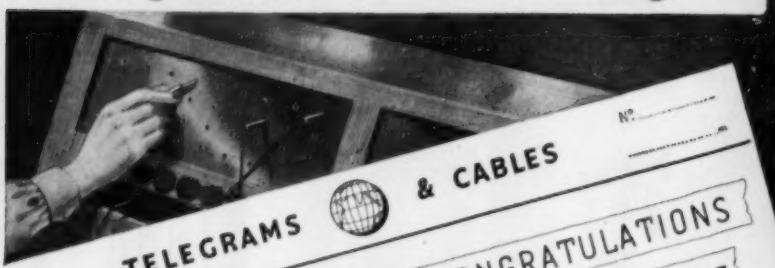

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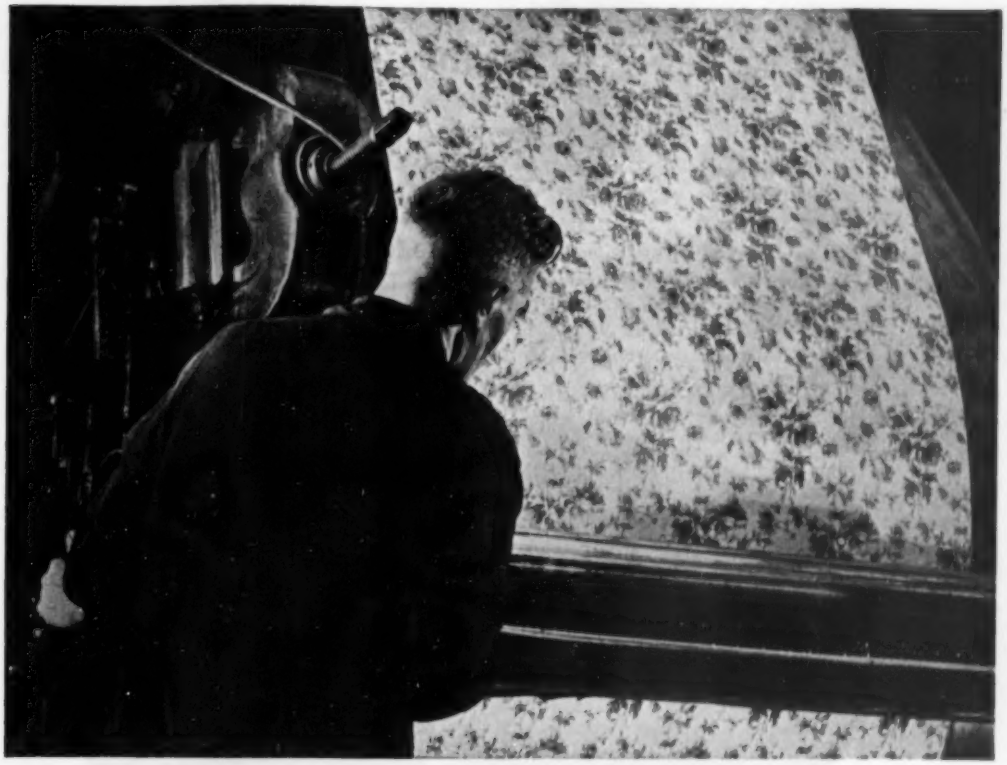

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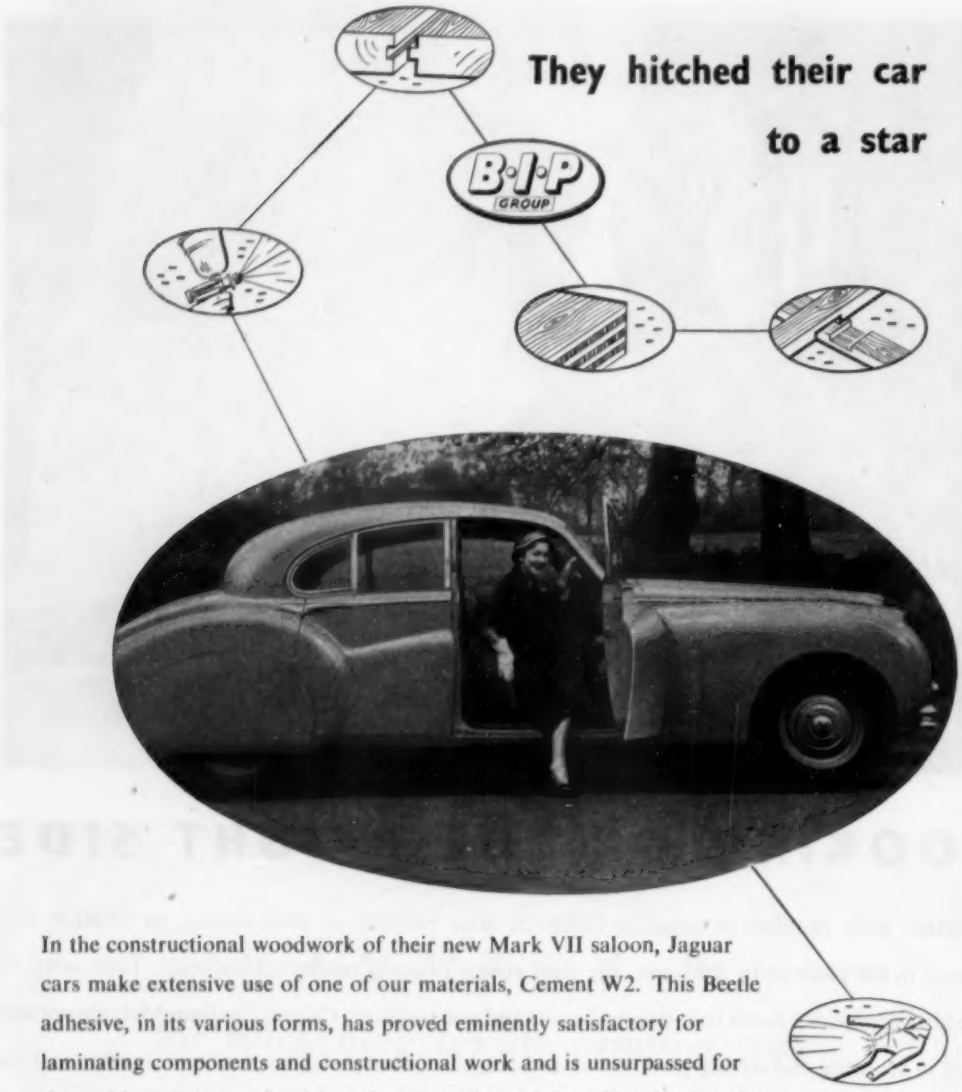

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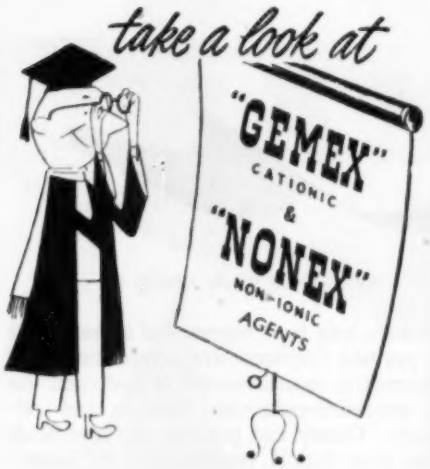

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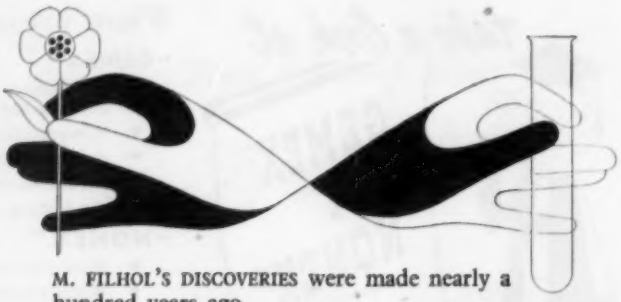

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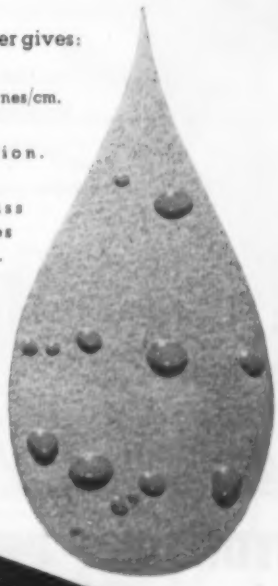

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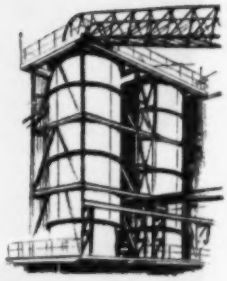

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